"DEVELOPMENT OF ELECTROCHEMICAL SENSOR FOR THE ELECTROCATALYTIC INVESTIGATION OF BIOLOGICALLY ACTIVE MOLECULES"

Final Synopsis of the Thesis Submitted to

MANGALORE UNIVERSITY

For the Fulfilment of the Award of Degree of

Doctor of Philosophy
in
Chemistry

Submitted by

Mr. HAREESHA N

Under the Supervision of

Dr. J G MANJUNATHA M.Sc., M.Phil., Ph.D.

Department of Chemistry,
Field Marshal K. M. Cariappa College,
A Constituent College of Mangalore University,
Kaveri Campus, Madikeri, Karnataka, India

October 2022

Name of Research Scholar:	Mr. HAREESHA. N
Place of Work:	Department of Chemistry, Field Marshal KM Cariappa College, Constituent College of Mangalore University, Madikeri, Karnataka, India.
Topic of research:	Development of electrochemical sensor for the electrocatalytic investigation of biologically active molecules
Name and address of the Guide:	Dr. J.G. Manjunatha, Assistant Professor, Department of Chemistry, Field Marshal KM Cariappa College, Constituent College of Mangalore University, Madikeri, Karnataka, India. Email: manju1853@gmail.com
Registration Number:	MU/EXB/Ph.D./CR.68/Chem./2020-21/E.13
Registration Date:	06/04/2018

Table of Contents

No.	Contents	Page No.
1	Introduction	1-2
2	Summary of the Thesis	2-3
3	Outline of the Thesis	3
4	Chapter 1	3
5	Chapter 2	4
6	Chapter 3	5
7	Chapter 4	6
8	Chapter 5	7
9	Chapter 6	8
10	Chapter 7	9
11	Chapter 8	10
12	Chapter 9	11
13	Chapter 10	12
14	References	13
15	List of Publications	14-17
16	List of Conference Attended	17-18
17	Publication First Pages	
18	Conference Certificates	

Introduction

Various organic molecules are present that are biologically and environmentally active and they characteristically show oxidation or reduction or redox reaction nature. These behaviours are most important in various biological and environmental activities, since, some selected molecules are electrochemically characterized based on their oxidation/reduction/redox characteristics. These electrochemical characteristics are encouraged the scholars to improve the electroanalytical methods and tools for the inspection of bioactive and electroactive molecules. The voltammetry is the electrochemical method concerning the documentation of current and potential response curves of bio or electroactive molecules on the surface of electrode material [1]. The basic principle concerned of in voltammetric technique is the conversion of chemical information into an electrical response, generally these progressions are taking place in an electrochemical compartment, which have the target bio or electroactive molecule (analyte) with the supporting electrolyte solution [2].

Voltammetry is the sensing methodology, which encompasses a broad range of vital applications involves, food and drug quality analysis, environmental monitoring, metal ions detection, agriculturally important and hazardous molecules detection, biological samples analysis, material characterisation and so on. The detailed purposes covering the development of electrochemical sensors, supercapacitors, fuel cells, batteries, and so on [3]. The cyclic voltammetry (CV) is a simple and easily adaptable electrochemical technique for scientific examination and development owed to the fact that the electrochemical reactions taken place at the electrode and solution interface can be inspected through this operation. It has imparted the essential evidence in various zones and will continue to assist the development of research as an electroanalytical tool. This technique provides an insight into the electron transfer kinetics and the electrochemical behaviour of molecule under study. Linear sweep voltammetry (LSV) is a voltammetric method where the current at a working electrode is measured while the potential between the working electrode and a reference electrode is swept linearly in time.

Oxidation or reduction of the species is registered as a peak or trough in the current signal at the potential at which the species begins to be oxidized or reduced [4]. Add-on to CV and LSV methods, differential pulse voltammetry (DPV) method is similarly used for the study of analytes with enhanced sensitivity and selectivity [5]. The electrochemical approaches are broadly utilised over other approaches such as chromatography, spectrometry, calorimetry, tandem mass spectrometry, chemiluminescence, capillary electrophoresis for the quantitative analysis of numerous molecules. Because, electrochemical approaches deliver higher sensitivity, sensible stability and accuracy, easiness in the preparation of working electrode, high linearity range, low-priced, less responsive towards atmospheric effect, lower consumption of reagents,

gives low limit of detection (LOD) and rapid response have incited the researcher's attention to use these methods [5].

Chemically modified electrodes have been resulted in both commercial and social benefits and are broadly operated in various applications such as safety, automotive, emissions monitoring, industrial hygiene, clinical diagnostics, process controls, and so on [6–10]. In that, carbon-based electrode materials are the most common self-made electrodes operated in the field of analytical and bioanalytical electrochemistry due to their simple preparation from a mixture of carbon powder or carbon nanotubes or graphene powder and a pasting liquid. Here, the carbon-based materials assist as a conducting electrode material [11]. The pasting liquid is of insulating character, assists as an inert medium and fixes distinct units into a condensed mixture [12]. The modified carbon-based electrodes possess numerous benefits like renewability, low background current, ease of fabrication, low-cost, stable response, and low ohmic resistance [13]. Different kinds of surface structures are being prepared through modification process. The different ways of modification technique include chemical modification, physical adsorption of surfactant molecules, electro-adsorption and electro-deposition through electro polymerization of monomer molecules [14,15]. Due to the modification, the electrode surface will be protected against non-electroactive interferents, which leads to decline the electrode response with time and it prohibits the analysis of untreated samples [16]. These types of modified electrode materials can be efficaciously applied for the trace analysis of electroactive molecules in commercial and real samples and also it eliminates the overlapping of analytical signals in simultaneous determination [17].

SUMMARY OF THE THESIS

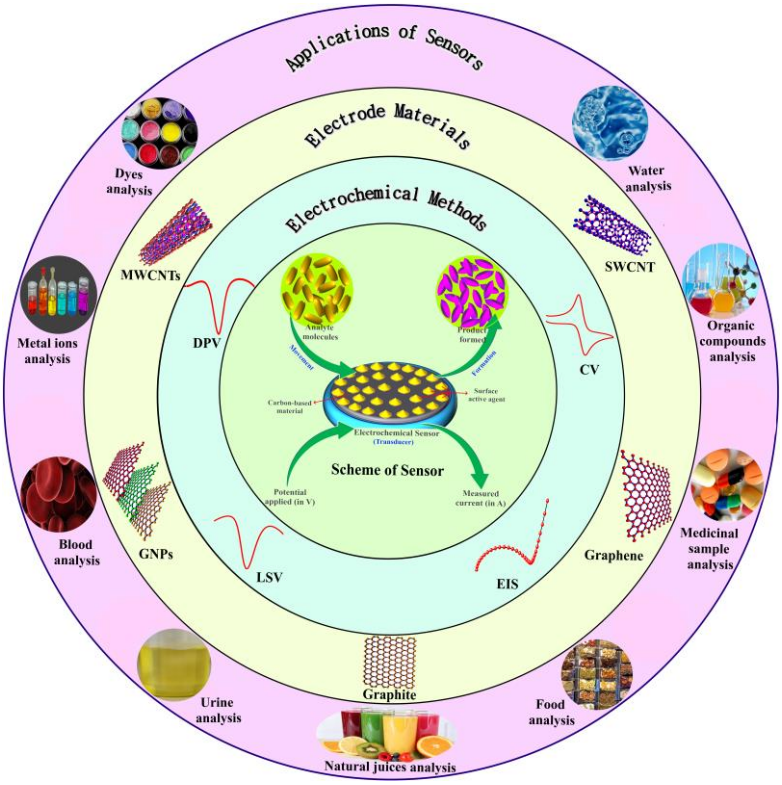
The present thesis conveys the effort made on the development of simple, eco-friendly, low-cost, and responsive electrochemical sensors for the detection of biologically and electrochemically active molecules in commercial and real samples (medicinal, environmental, biological, and food samples). The performed research effort involved the construction of carbon and carbon composite (carbon powder, graphite powder, MWCNTs, CNTs, GNPs, and their composite) paste electrode materials for the electrochemical analysis of several biologically important molecules using different voltammetric methods such as LSV, CV, and DPV. Also, the electrocatalytic nature of the unmodified electrode surfaces was improved using the chemical surface-active agents based on the following methods such as electrochemical deposition or electrochemical polymerization, immobilization of surfactant, and acid/base treatment. The prepared carbon and carbon composite paste electrode materials were characterized using CV, EIS, FE-SEM, and EDX methods.

The described research effort validates an acceptable contribution to the pursuit of innovative and simplest electroanalytical approaches applicable for commercial and real samples analysis. The electrochemically and biologically reactive and important organic molecules like RTN, VL, RF, FLFT, DA, IC, AMX, and CL were examined using different carbon-based electrochemical sensors. Here, the significant applications were experimented like oxidation and reduction reaction nature, number of electrons and protons transfer, heterogeneous rate constant of the reaction, nature of the electrode, sensitivity, selectivity, repeatability, and reproducibility of the electrode material for the analysis of electrochemically and biologically reactive and important organic molecules. Additionally, the projected approach was operated for the analysis of various real samples like food, environmental, medicinal, and biological samples.

OUTLINE OF THE THESIS

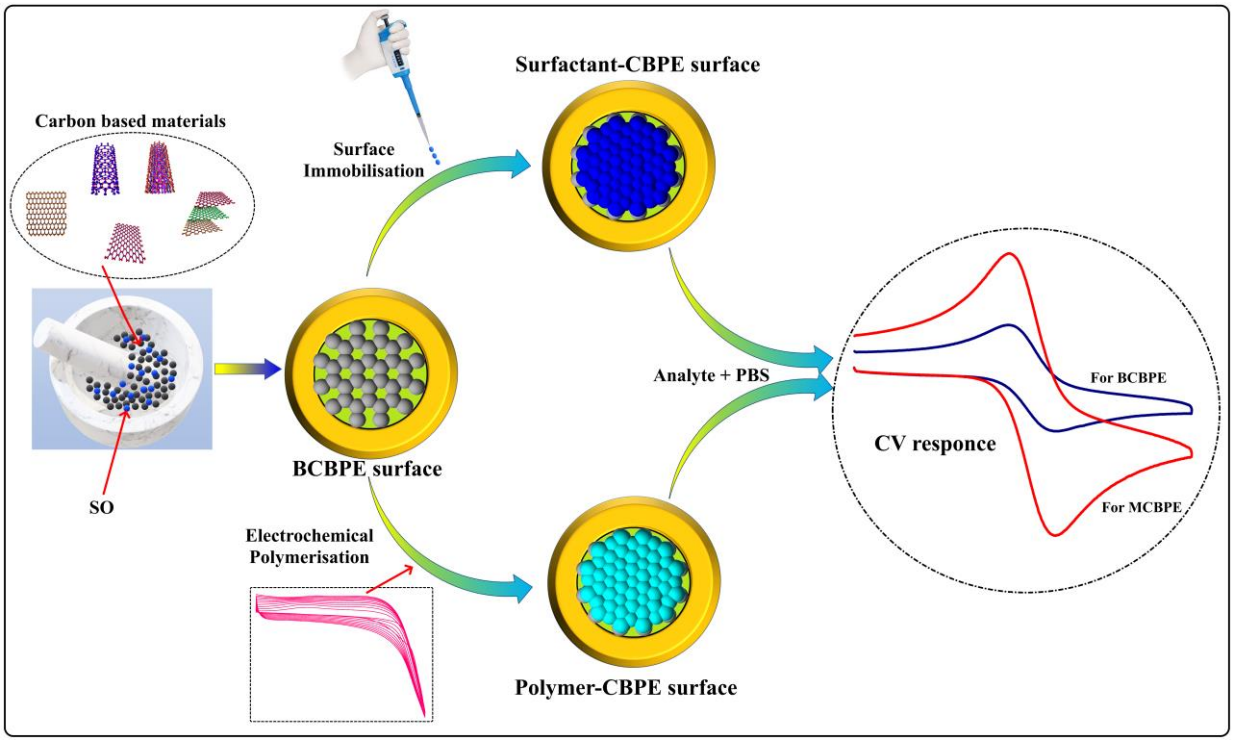
The thesis entitled "Development of electrochemical sensor for the electrocatalytic investigation of biologically active molecules" has been divided into '10 Chapters' are as follows,

Chapter 1: Introduction to Electrochemical Sensors and Voltammetry for the Detection and Quantification of Biologically Active Molecules



This chapter gives a detailed introduction about Electrochemical sensors, biologically active molecules, carbon-based materials, different voltammetric techniques, theoretical background, advantages and their applications. This chapter also provides a concise review of the literature related to various electrochemical sensors developed for the analysis of different biologically active molecules.

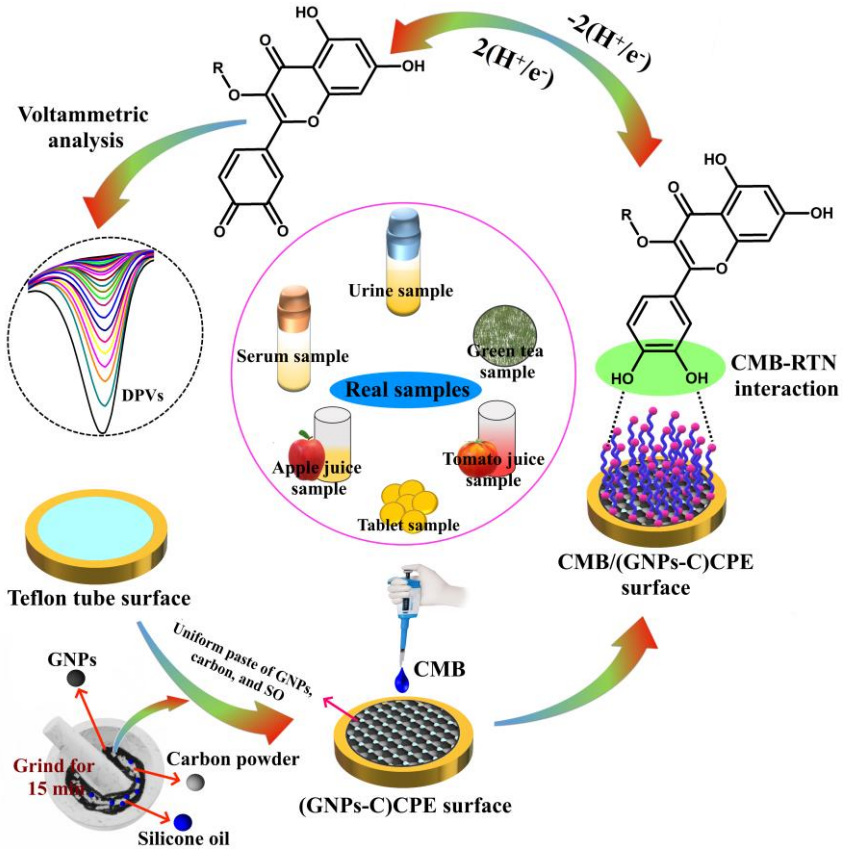
Chapter 2: Experimental: Materials and Methods



This chapter explains a brief account of the materials, instruments, and methods used in our research work. Also, it describes the procedures implemented for the preparation of chemically modified electrochemical sensors for the analysis of some biologically and electrochemically active molecules.

Chapter 3: Simple and Affordable Graphene Nano-Platelets and Carbon Composite Surface Decorated with Cetrimonium Bromide as a Responsive Electrochemical Sensor for Rutin Detection

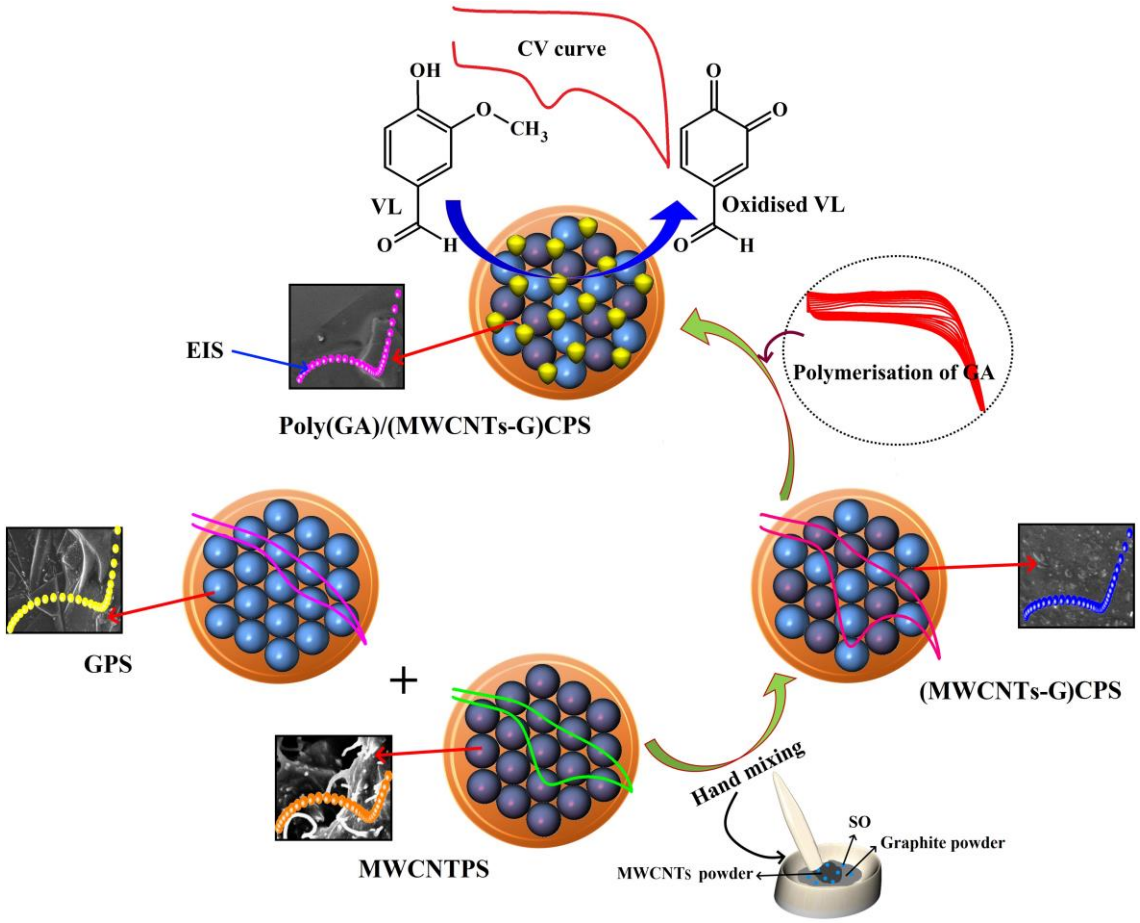
Journal of Electroanalytical Chemistry, 917 (2022) 116388. IF=4.598.



In this research work, an economical, efficient, and unfussy nanocomposite sensor was equipped for the analysis of powerful antioxidant RTN. Due to the synergetic effect with more surface-active sites, CMB was decorated on the surface of nanocomposite of GNPs and carbon paste to attribute a superior electro-catalytic nature for RTN detection in PBS as a supporting electrolyte. The proposed CMB/(GNPs-C)CPE declines the material resistance and overpotential with rising the kinetic rate, peak currents, and material conductance towards the RTN detection. In the optimal experimental conditions, the analysing efficiency of CMB/(GNPs-C)CPE was examined using the LSV, CV, and DPV with a finer linear relation, and the corresponding LOD values are found to be 0.041 µM, 0.023 µM, and 0.002 µM, respectively. The effect of some organic molecules and some metal ions on RTN detection at CMB/(GNPs-C)CPE was studied with acceptable results. The sensitivity, selectivity, steadiness, repeatability, and reproducibility of the modified sensor were studied with decent results. The practicability of CMB/(GNPs-C)CPE was verified by analysing RTN in blood serum, urine, green tea, tomato juice, apple juice, and medicinal samples with adequate recoveries.

Chapter 4: A Fast and Selective Electrochemical Detection of Vanillin in Food Samples on the Surface of Poly(Glutamic Acid) Functionalized Multiwalled Carbon Nanotubes and Graphite Composite Paste Sensor

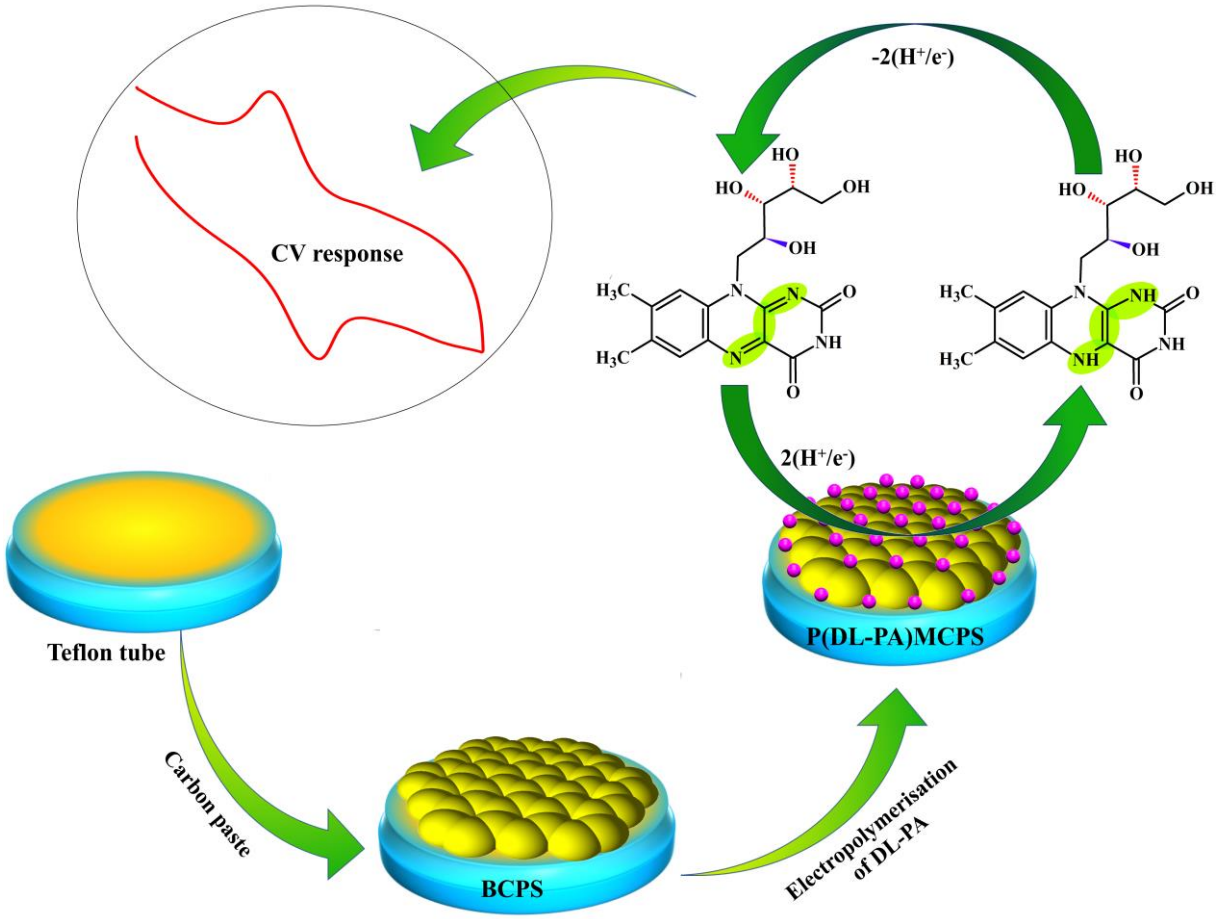
Colloids and Surfaces A: Physicochemical and Engineering Aspects, 626 (2021) 127042. IF:5.518.



In this research work, the electrochemical oxidation of VL in 0.2 M PBS of pH 6.5 was determined in food samples using an electrochemically polymerized GA functionalized MWCNTs and graphite composite paste sensor (P(GA)/(MWCNT-G)CPS). The surface concert and morphology of the sensing materials were examined using FE-SEM, EIS, and CV measurements. The electrochemical oxidation kinetics of VL was discussed using parameters like solution pH, potential scan rate, temperature, concentration, accumulation potential, and accumulation time. The selective electrochemical oxidation of VL was analysed in the presence of metal ions, organic dyes, and sugars on the surface of the functionalized composite sensor. The modified sensor provides a fine linear dynamic range (0.50 to 18.0 μM) for the electrochemical oxidation of VL with a low LOD of 0.019 μM. The DPV measurement was performed for the analysis of VL in food samples with adequate recoveries. Further, the equipped sensor needs lesser preparation cost and presents good reliability, conductivity, repeatability, sensitivity, and reproducibility towards the electrochemical oxidation of VL.

Chapter 5: A simple and Low-cost Poly(DL-Phenylalanine) Modified Carbon Sensor for the Improved Electrochemical Analysis of Riboflavin

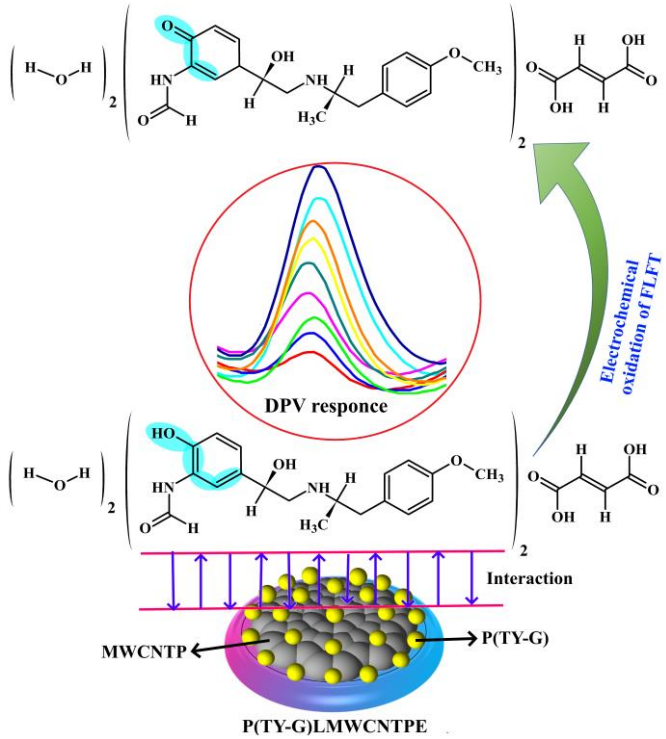
Journal of Science: Advanced Materials and Devices, 5 (2020) 502-511. IF:7.382.



This research work reports the electroanalysis of RF on the surface of a P(DL-PA)MCPS. The developed sensor caused a noticeable electrocatalytic action for the redox activity of RF in PBS of pH 6.5. This analysis was evaluated using DPV and CV techniques. The active surface of the functioning sensor exposes well developed anodic peak with prominent electron transfer. P(DL-PA)MCPS shows distinctive and improved DPV and CV peaks for RF with and without the presence of DA. The impact of the solution pH, potential scan rate, accumulation potential and concentration on RF at P(DL-PA)MCPS were studied. A vibrant linear growth was observed between the oxidation peak current and the RF concentration in the range of 6.0 to 30.0 µM which provides a lower LOD of 92 nM with excellent sensitivity. The proposed method and sensor were applied for the assessment of RF in medicine sample as an analytical application with fine recoveries and low LOD.

Chapter 6: Electro-Oxidation of Formoterol Fumarate on Novel Poly(Thiazole Yellow-G) Layered Multi-Walled Carbon Nanotube Paste Electrode

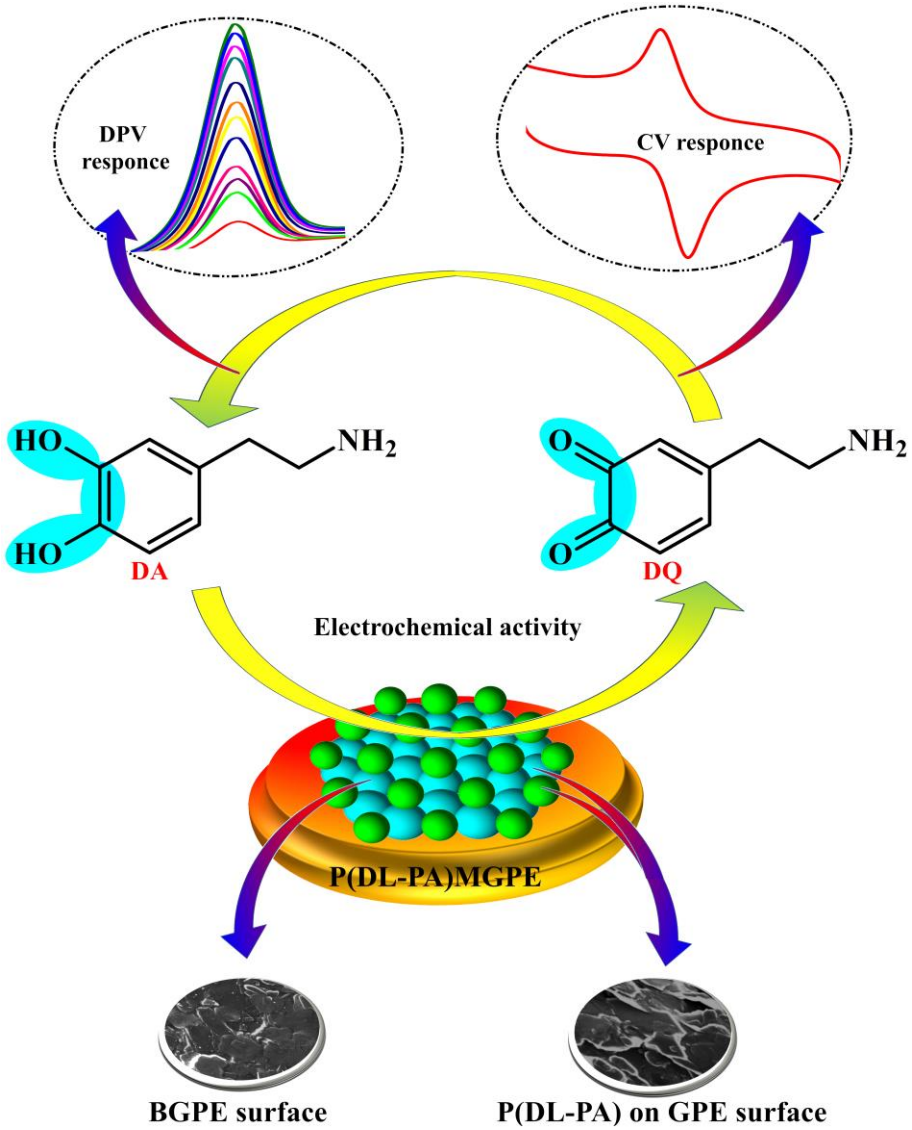
Scientific Reports, 11 (2021) 12797. IF: 4.996.



This research work explains the electro-oxidation behaviour of FLFT in the presence of UA on the surface of P(TY-G)LMWCNTPE. The modified (P(TY-G)LMWCNTPE) and unmodified (MWCNTPE) electrode materials were characterized through EIS, FE-SEM, CV, and DPV approaches. The characterization data confirms the good conducting and electrocatalytic nature with more electrochemical active sites on the P(TY-G)LMWCNTPE than MWCNTPE towards the FLFT analysis in the presence of UA. P(TY-G)LMWCNTPE easily separates the two drugs (FLFT and UA) even though they both have nearer oxidation peak potential. The electro-catalytic activity of the developed electrode is fast and clear for FLFT electro-oxidation in 0.2 M PBS of pH 6.5. The P(TY-G)LMWCNTPE offered a well-resolved peak with the highest electro-oxidation peak current at the peak potential of 0.538 V than MWCNTPE. The potential scan rate and oxidation peak growth time studies show the electrode reaction towards FLFT electro-oxidation is continued through a diffusion-controlled step. The variation of concentration of FLFT in the range from 0.2 to 1.5 µM (absence of UA) and 3.0 to 8.0 µM (presence of UA) provides a good linear relationship with increased peak current and a lower LOD values of 0.0128 µM and 0.0129 µM, respectively. The prepared electrode gives a fine recovery for the detection of FLFT in the medicinal sample with acceptable repeatability, stability, and reproducibility.

Chapter 7: Fast and Enhanced Electrochemical Sensing of Dopamine at Cost-effective Poly(DL-Phenylalanine) Based Graphite Electrode

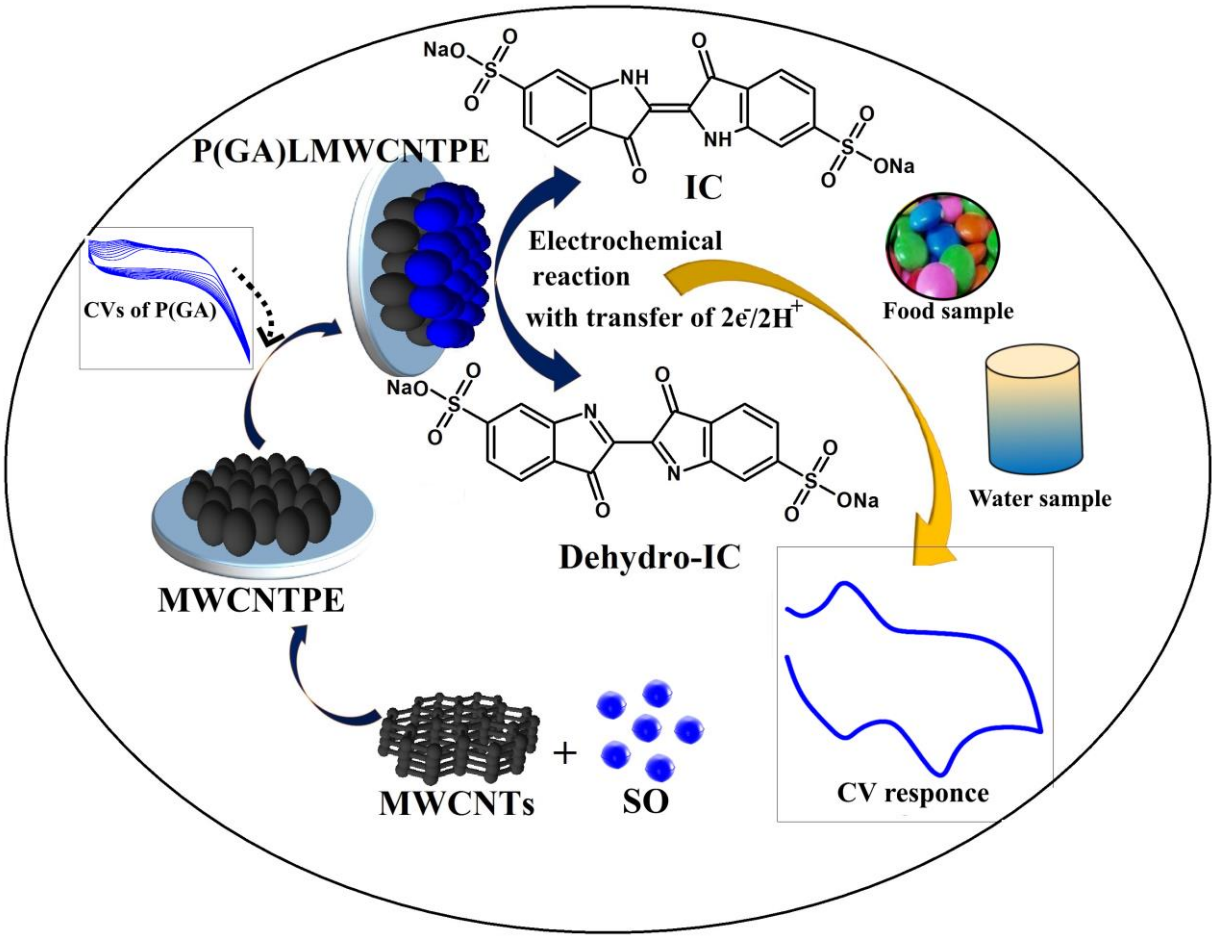
Journal of Electroanalytical Chemistry, 878 (2020) 114533. IF:4.598.



In this research work, a sensitive and low-priced P(DL-PA)MGPE was designed for the analysis of DA. The redox activity of DA in PBS of pH 6.5 was inspected at the developed electrode using CV and DPV methods. The voltammetric results present that the P(DL-PA)MGPE exposes a significant enrichment in DA redox currents with the declining of overpotential than the BGPE. In the optimal operating conditions, P(DL-PA)MGPE describes a fine linear enhancement for DA oxidation in the concentration range of 2.0 to 45.0 μM with an estimated lower LOD of 28.0 nM and LOQ of 93.0 nM. The proposed electrode shows good selectivity and sensitivity for DA analysis in the presence of interfering moieties such as AA and UA. Finally, the prepared sensor was potentially used for the actual DA detection in the medicinal sample.

Chapter 8: Electrochemical Analysis of Indigo Carmine in Food and Water Samples Using a Poly(Glutamic Acid) Layered Multi-Walled Carbon Nanotube Paste Electrode

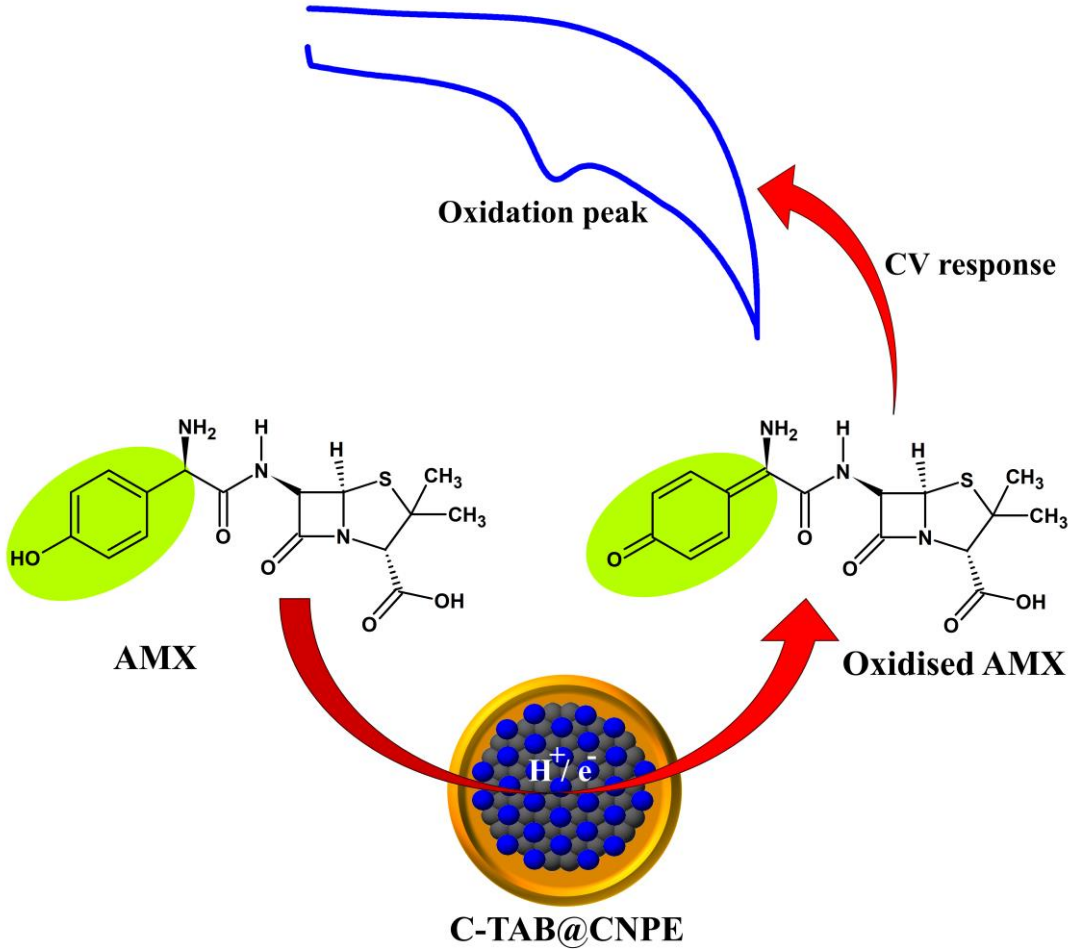
Journal of Electronic Materials, 50 (2021) 1230–1238. IF:2.047.



In this research work, a modest electrochemically polymerized GA layered MWCNTP electrode was functionalized for the sensing of IC by powerful DPV and CV approaches. Within the optimized experimental conditions, the P(GA)LMWCNTPE holds an acceptable and high rate of electro-catalytic activity towards the redox behaviour of IC. The projected P(GA)LMWCNTPE shows a decent selectivity for IC in the presence of MO. The modified sensor shows an acceptable linear growth between oxidative peak current and concentration in both CV and DPV methods with fine LOD values of 4.2 µM and 0.36 µM, respectively. Additionally, the developed sensor was effectively applied to detect IC in food and water samples. The morphological and surface activities of the modified and unmodified electrodes were determined through FE-SEM, EIS, and CV techniques. The P(GA)LMWCNTPE requires a simple preparation procedure and low-cost with acceptable storage stability, sensitivity, and reproducibility.

Chapter 9: Electrochemical Sensing of Amoxicillin at Simple and Selective Carbon Paste Electrode Activated with Cetrimonium Bromide Surfactant

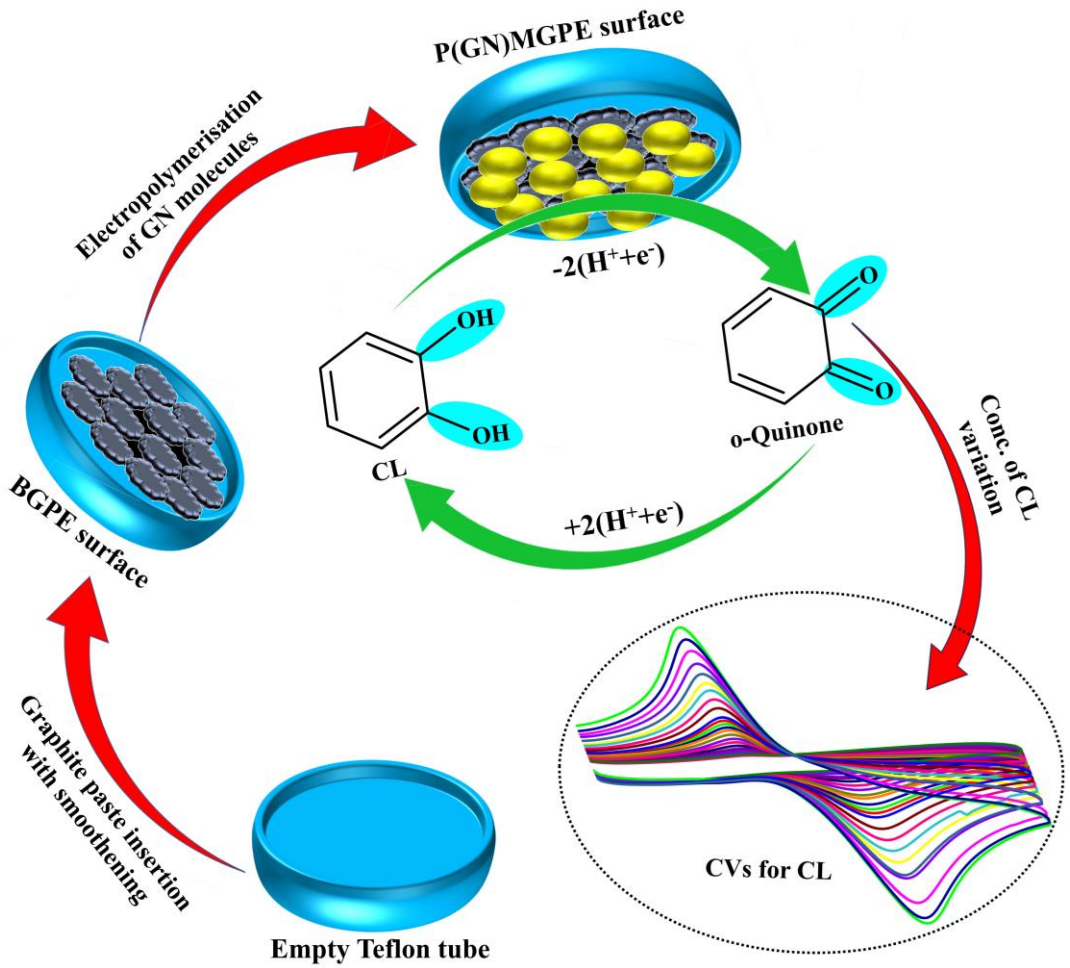
Monatshefte für Chemie-Chemical Monthly, 153 (2022) 31–38. IF:1.613.



In this research work, the operative, selective, and electrochemically steady CMB drop-casted CPE was constructed for the detection of AMX in presence of DA through the CV method. The modified and unmodified electrode materials were characterized by various methods like FE-SEM, CV, and EIS with acceptable results. The constructed modified sensor delivers a higher electrocatalytic nature for the oxidation of 0.1 mM AMX in 0.1 M PBS of 6.5 pH with high peak current and lower peak potential than the BCPE. The analytical applicability of modified electrode for AMX electro-oxidation was detected by increasing the AMX concentration in the range from 10.0 to 150.0 µM with fine LOD and LOQ of 5.90 µM and 19.67 µM, respectively. This article discloses a facile approach for the concurrent inspection of AMX in presence of DA. The modified sensor gives high stability, repeatability, reproducibility, and sensitivity. The operated method and modified sensor give a fine recovery for AMX detection in medication sample.

Chapter 10: Simple and Green Electrochemically Polymerized Glutamine Activated on Graphite Paste Surface as a Biosensor for Sensitive Catechol Detection

Accepted in Journal of Materials Science: Materials in Electronics, (2022). IF: 2.779



In this research work, an electrochemically polymerized GN clustered GPE surface was developed for the electrochemical detection of hazardous CL molecules. The CV method was operated for the detection of redox activities of CL in PBS of pH 7.0 on the surface of P(GN)MGPE. The EIS, FE-SEM, EDX, and CV methods were used to elucidate the surface behaviours and morphology of the prepared electrode materials. The P(GN)MGPE provides a well-defined and highly sensitive electrochemical redox peak for CL based on an adsorption-controlled reaction approach compared to the BGPE surface. The activated electrochemical sensor provides good linear relation among the concentrations, and the corresponding reduction peak currents of CL ranging from 2.0 to 200.0 µM and the calculated LOD and LOQ are found to be 0.045 µM and 0.151 µM, respectively. The activated electrode surface reveals high electrocatalytic activity with good reproducibility, repeatability, and stability. Finally, the P(GN)MGPE surface was operated for the detection of CL in water samples with a fine recovery ranging from 99.23 to 100.42%.

References

[1] Petr Zuman, *FABAD J. Pharm. Sci*. 31 (2006) 97–115.

[2] C. B. Braungardt, *Anal. Methods*. 7 (2015) 1249–1260.

[3] J. Wang, Analytical Electrochemistry, Wiley-VCH, Weinheim, (2006).

[4] F. J. Thomas, G. Henze, Applications: Organic species, Introduction to Voltammetric Analysis: Theory and Practice, CSIRO Publishing, (2001).

[5] M. Elysi, M. A. Khalilzadeh, *Food Chem.* 141 **(2013)** 4311–4317.

[6] J. K. Campbell, L. Sum, R. M. Crooks, *J. Am. Chem. Soc*. 121 (1999) 3779–3780.

[7] Joseph, Z. Stetter, W. R. Penrose, S. Yao, *J. Electrochem. Soc*. 150 (2003) S11–S16.

[8] A. Lindgren, J. Emnéus, T. Ruzgas, L. Gorton, G. Marko-Varga, *Anal. Chim. Acta*. 347 (1997) 51–62.

[9] W. Sun, Q. Jiang, K. Jiao, *J. Solid State Electrochem*. 13 (2009) 1193–1199.

[10] F. Manea, A. Pop, C. Radovan, P. Malchev, A. Bebeselea, G. Burtica, S. Picken, J. Schoonman, *Sensors*. 8 **(**2008) 5806–5819.

[11] D. Bellido-Milla, L. M. Cubillana-Aguilera, M. E. Kaoutit, M. P. Hernández-Artiga, J. L. Hidalgo-Hidalgo de Cisneros, I. Naranjo-Rodríguez, J. M. Palacios-Santander, *Anal. Bioanal. Chem*. 405 (2013) 3525–3539.

[12] I. Švancara, A. Walcarius, K. Kalcher, K. Vytřas, *Cent. Eur. J. Chem*. 7 (2009) 598–656.

[13] C. Oueiny, S. Berlioz, F. X. Perrin, *Prog. Polym. Sci*. 39 (2014) 707–748.

[14] H. J. Jeon, S. C. Yi, S. G. Oh, *Biomaterials* 24 (2003) 4921–4928.

[15] J. M. Zen, A. S. Kumar, D. M. Tsai, *Electroanalysis*. 15 (2003) 1073–1087.

[16] M. A. T. Gilmartin, J. P. Hart, *Analyst*. 120 (1995) 1029–1045.

[17] M. R. Akhgar, H. Beitollahi, M. Salari, H. Karimi-Maleh, H. Zamani, *Anal. Methods*, 4, (2012) 259–264.

LIST OF PUBLICATIONS

[1] **N. Hareesha**, J.G. Manjunatha, Z.A. Alothman, M. Sillanpää, Simple and affordable graphene nano-platelets and carbon nanocomposite surface decorated with cetrimonium bromide as a highly responsive electrochemical sensor for rutin detection, Journal of Electroanalytical Chemistry, 2022, 917, 116388.

[2] **N. Hareesha**, J.G. Manjunatha, B.M. Amrutha, N. Sreeharsha, S.M. Basheeruddin Asdaq, Md Khalid Anwer, A fast and selective electrochemical detection of vanillin in food samples on the surface of poly(glutamic acid) functionalized multiwalled carbon nanotubes and graphite composite paste sensor, Colloids and Surfaces A: Physicochemical and Engineering Aspects, 2021, 626, 127042.

[3] **N. Hareesha**, J.G. Manjunatha, A simple and low-cost poly(dl-phenylalanine) modified carbon sensor for the improved electrochemical analysis of Riboflavin, Journal of Science: Advanced Materials and Devices, 2020, 5, 502-511.

[4] **N. Hareesha**, J.G. Manjunatha, Electro-oxidation of formoterol fumarate on the surface of novel poly(thiazole yellow-G) layered multi-walled carbon nanotube paste electrode, Scientific Reports, 2021, 11, 12797.

[5] **N. Hareesha**, J.G. Manjunatha, Fast and enhanced electrochemical sensing of dopamine at cost-effective poly(dl-phenylalanine) based graphite electrode, Journal of Electroanalytical Chemistry, 2020, 878, 114533.

[6] **N. Hareesha**, J.G. Manjunatha, B.M. Amrutha, P.A. Pushpanjali, M.M. Charithra, N.S. Prinith, Electrochemical analysis of indigo carmine in food and water samples using a poly(glutamic acid) layered multi-walled carbon nanotube paste electrode, Journal of Electronic Materials, 2021, 50, 1230-1238.

[7] **N. Hareesha**, J.G. Manjunatha, P.A. Pushpanjali, N. Prinith Subbaiah, M.M. Charithra, N. Sreeharsha, S.M. Basheeruddin Asdaq, Md. Khalid Anwer, Electrochemical sensing of antibiotic drug amoxicillin in the presence of dopamine at simple and selective carbon paste electrode activated with cetyltrimethylammonium bromide surfactant, Monatshefte für Chemie - Chemical Monthly, 2022, 153, 31-38.

[8] **N. Hareesha**, J.G. Manjunatha, Elevated and rapid voltammetric sensing of riboflavin at poly(helianthin dye) blended carbon paste electrode with heterogeneous rate constant elucidation, Journal of the Iranian Chemical Society, 2020, 17, 1507-1519.

[9] **N. Hareesha**, J.G. Manjunatha, C. Raril, G. Tigari, Sensitive and selective electrochemical resolution of tyrosine with ascorbic acid through the development of electropolymerized alizarin

sodium sulfonate modified carbon nanotube paste electrodes, ChemistrySelect, 2019, 4, 4559-4567.

[10] **N. Hareesha**, J.G. Manjunatha, Surfactant and polymer layered carbon composite electrochemical sensor for the analysis of estriol with ciprofloxacin, Materials Research Innovations, Materials Research Innovations, 2020, 24, 349–362.

[11] **N. Hareesha**, J.G. Manjunatha, C. Raril, G. Tigari, Design of novel surfactant modified carbon nanotube paste electrochemical sensor for the sensitive investigation of tyrosine as a pharmaceutical drug, Advanced Pharmaceutical Bulletin, 2019, 9, 132-137.

[12] **N. Hareesha**, J.G. Manjunatha, A.A. Al-Kahtani, A.M. Tighezza, N. Ataollahi, electrochemical determination of riboflavin using a poly(titan yellow) modified carbon nanotube paste electrode in the presence of dopamine, ChemistrySelect, 2022, 7, e202200537.

[13] B.M. Amrutha, J.G. Manjunatha, S. Aarti Bhatt, **N. Hareesha**, Sensitive and selective electrochemical detection of vanillin at graphene based poly(methyl orange) modified paste electrode, Journal of Science: Advanced Materials and Devices, 2021, 6, 415-424.

[14] P.A. Pushpanjali, J.G. Manjunatha, **N. Hareesha**, E.S. D'Souza, M.M. Charithra, N.S. Prinith, Voltammetric analysis of antihistamine drug cetirizine and paracetamol at poly(L-Leucine) layered carbon nanotube paste electrode, Surfaces and Interfaces, 2021, 24, 101154.

[15] P.A. Pushpanjalia, J.G. Manjunatha, **N. Hareesha**, B.M. Amrutha, C. Raril, Z.A. ALOthman, A.M. Alanazi, A. Pandith, Fabrication of poly(ʟ-Aspartic acid) Layer on graphene nanoplatelets paste electrode for riboflavin sensing, Materials Chemistry and Physics, 2022, 276, 125392.

[16] P.A. Pushpanjalia, J.G. Manjunatha, **N. Hareesha**, T. Girish, A.A. Al-Kahtani, A.M. Tighezza, N, Ataollahi, Electrocatalytic determination of hydroxychloroquine using sodium dodecyl sulphate modified carbon nanotube paste electrode, Topics in Catalysis, 2022. DOI:10.1007/s11244-022-01568-8.

[17] B.M. Amrutha, J.G. Manjunatha, A.S. Bhatt, **N. Hareesha**, A.A. Al-Kahtani, A.M. Tighezza, N, Ataollahi, Electrocatalytic analysis of diclofenac in the presence of dopamine at surface amplified voltammetric sensor based on poly(glycine) modified carbon nano tube paste electrode, Topics in Catalysis, 2022. DOI:10.1007/s11244-022-01567-9.

[18] P.A. Pushpanjalia, J.G. Manjunatha, **N. Hareesha**, An overview of recent developments of carbon-based sensors for the analysis of drug molecules, Journal of Electrochemical Science and Engineering, 2021, 11, 161-177.

[19] N.S. Prinith, J.G. Manjunatha, **N. Hareesha**, Electrochemical validation of L-tyrosine with dopamine using composite surfactant modified carbon nanotube electrode, Journal of the Iranian Chemical Society, 2021, 18, 3493-3503.

[20] J.G. Manjunatha, C. Raril, N.S. Prinith, P.A. Pushpanjali, M.M. Charithra, Girish Tigari, **N. Hareesha**, Edwin S. D'Souza, B.M. Amrutha, Fabrication, characterization and application of poly(acriflavine) modified carbon nanotube paste electrode for the electrochemical determination of catechol, Handbook of Nanomaterials for Sensing Applications Micro and Nano Technologies, Elsevier, 2021, 105-117.

[21] T. Girish, J.G. Manjunatha, C. Raril, **N. Hareesha**, Determination of riboflavin at carbon nanotube paste electrodes modified with an anionic surfactant, ChemistrySelect. 2019, 4, 2168-2173.

[22] P.A. Pushpanjali, J.G. Manjunatha, B.M. Amrutha, **N. Hareesha**, Development of carbon nanotube-based polymer-modified electrochemical sensor for the voltammetric study of Curcumin, Materials Research Innovations, 2020, 25, 412-420.

[23] M.M. Charithra, J.G. Manjunatha, N.S. Prinith, P.A. Pushpanjali, T. Girish, **N. Hareesha**, Electroanalytical determination of tinidazole by using surface modified carbon nano composite based sensor, Materials Research Innovations, 2022, 26, 285-294.

[24] D.N. Varun, J.G. Manjunatha, **N. Hareesha**, S. Sandeep, P. Mallu, C.S. Karthik, N.S. Prinith, N. Sreeharsha, S.M. Basheeruddin Asdaq, Simple and sensitive electrochemical analysis of riboflavin at functionalized carbon nanofiber modified carbon nanotube sensor, Monatshefte für Chemie - Chemical Monthly, 2021, 152, 1183-1191.

[25] G. Tigari, J.G. Manjunatha, E.S. D' Souza, C. Raril, **N. Hareesha**, M.M. Charithra. Electrochemical determination of levofloxacin drug at poly(clayton yellow)/carbon paste electrode, Monatshefte für Chemie - Chemical Monthly, 2022, 153, 311-319.

[26] Girish Tigari, J.G. Manjunatha, **N. Hareesha**, N.S. Prinith, Research developments in carbon materials-based sensors for determination of hormones, Journal of Electrochemical Science and Engineering, 2022, 12, 3-23.

[27] J.G. Manjunatha, C. Raril, **N. Hareesha**, M.M. Charithra, P.A. Pushpanjali, G. Tigari, D.K. Ravishankar, S.C. Mallappaji, J. Gowda, Electrochemical fabrication of poly(niacin) modified graphite paste electrode and its application for the detection of riboflavin, The Open Chemical Engineering Journal, 2021, 14, 90-98.

[28] B.M. Amrutha, J.G. Manjunatha, S. Aarti Bhatt, **N. Hareesha**, Electrochemical analysis of evans blue by surfactant modified carbon nanotube paste electrode, Journal of Materials and Environmental Science, 2019, 10, 668-676

[29] T. Girish, J.G. Manjunatha, C. Raril, **N. Hareesha**, Electrochemical determination of resorcinol with tartrazine at non-ionic surfactant modified graphite powder and carbon nanotube composite paste electrode, Drug Design Open Access Journals, 2019, 4, 1-5.

[30] C. Raril, J.G. Manjunatha, T. Girish, **N. Hareesha**, Fabrication of the tartrazine voltammetric sensor based on surfactant modified carbon paste electrode, Open Access Journal of Chemistry, 2018, 2, 21-26.

PAPERS PRESENTED IN CONFERENCES

[1] **N. Hareesha** and J.G. Manjunatha, Electrochemical investigation of l-tyrosine using surfactant modified carbon nanotube paste electrode-a cyclic voltammetry. The International Conference on Nanotechnology-2019 "Opportunities and Challenges" organized by UG and PG Departments of Chemistry in association with the University of Namur, Belgium at St Aloysius College, Mangalore, Karnataka, India (10^{th} & 11^{th} January 2019).

[2] **N. Hareesha** and J.G. Manjunatha, Electrochemical investigation of riboflavin using sensitive polymerized methyl orange modified carbon paste electrode. "National Conference on Recent Advances in Material Science" organized by Deportment of Chemistry, Field Marshal K. M. Cariappa College (Affiliated to Mangalore University), Madikeri, Karnataka, India (5^{th} February 2019).

[3] **N. Hareesha** and J.G. Manjunatha, Electrochemical analysis of Vitamin B2 using Polymerized Graphite Paste Electrode. "National Symposium on Recent Advances at the Interface between Chemical & Biological Sciences" organized by Deportment of Chemistry and Biochemistry, Indian Academy Degree College Autonomous (Affiliated to Bangalore North University), Bangalore, Karnataka, India (29^{th} July 2019).

[4] **N. Hareesha** and J.G. Manjunatha, Surfactant and polymer modified carbon composite senor for the determination of estriol, "National Conference on Advanced Materials for Health, Energy & Environment" organized by Deportment of Chemistry, JSS Science and Technology University, Mysore, Karnataka, India (6^{th} & 7^{th} September 2019).

[5] **N. Hareesha** and J.G. Manjunatha, Polymer doped carbon paste electrode for the analysis of dopamine. "National Seminar on Current Trends in Chemical Research and Development" organized by Deportment of Chemistry, Vivekanada College of Arts, Science and Commerce, Puttur, Karnataka, India (18^{th} September 2019).

[6] **N. Hareesha** and J.G. Manjunatha, SDS and xanthacridinum modified carbon composite sensor for the investigation of estriol. "International Conference on advances in chemical and materials sciences" organized by Deportment of Studies in Chemistry, Mangalore University, Karnataka, India (17^{th} to 19^{th} October 2019).

[7] **N. Hareesha** and J.G. Manjunatha, Voltammetric analysis of lactoflavin at poly (phenylalanine) modified carbon paste electrode. "International Conference on life, chemical, and health Science" organized by Deportment of Life Sciences, Ramaiah College of Arts, Science & Commerce, Karnataka, India (24^{th} to 26^{th} October 2019).

[8] **N. Hareesha** and J.G. Manjunatha, Electrochemical analysis of indigo carmine at polymer layered carbon nanotube paste electrode. "Conference on Electrochemistry for Industry, Health and Environment" organized by BARC, Mumbai, India (21^{st} to 25^{th} January 2020)

[9] **N. Hareesha** and J.G. Manjunatha, Electrochemical study of estriol using surfactant and poly (acriflavine) doped carbon-carbon nanotube composite sensor. "Recent Novel Approaches in Chemical Sciences" organized by Deportment of Chemistry, Field Marshal K. M. Cariappa College (Affiliated to Mangalore University), Madikeri, Karnataka, India (12^{th} February 2020).

Research Scholar
(Hareesha N)

Research Guide
(Dr. J. G. Manjunatha)

PUBLICATIONS

Journal of Electroanalytical Chemistry 917 (2022) 116388

Contents lists available at ScienceDirect

Journal of Electroanalytical Chemistry

journal homepage: www.elsevier.com/locate/jelechem

Simple and affordable graphene nano-platelets and carbon nanocomposite surface decorated with cetrimonium bromide as a highly responsive electrochemical sensor for rutin detection

N. Hareesha [a], J.G. Manjunatha [a,*], Zeid A. Alothman [b], Mika Sillanpää [c]

[a] Department of Chemistry, FMKMC College, Constituent College of Mangalore University, Madikeri, Karnataka, India
[b] Department of Chemistry, College of Science, King Saud University, Riyadh 11451, Saudi Arabia
[c] Department of Biological and Chemical Engineering, Aarhus University, Norrebrogade 44, 8000, Aarhus C, Denmark

ARTICLE INFO

Keywords:
Rutin
Graphene nanoplatelets
Carbon paste electrode
Cetrimonium bromide
Electrochemical analysis
Biological and Food samples

ABSTRACT

In this article, an economical, efficient, and unfussy nanocomposite sensor was equipped for the analysis of powerful antioxidant rutin (RTN). Due to the synergetic effect with more surface-active cites, cetrimonium bromide (CMB) was decorated on the surface of nanocomposite of graphene nano-platelets (GNPs) and carbon (CB) paste to attribute a superior electro-catalytic nature for RTN detection in phosphate buffer (PB) as a supporting electrolyte. The proposed CMB functionalized GNPs-CB composite paste electrode (CMB/GNPs-CBCPE) declining the material resistance and overpotential with rising the kinetic rate, peak currents, and material conductance towards the RTN detection. In the optimal experimental conditions, the analyzing efficiency of CMB/GNPs-CBCPE was examined using the linear sweep voltammetry (LSV), cyclic voltammetry (CV), and differential pulse voltammetry (DPV) with a finer linear relation andthe corresponding limit of detection (LOD) values are found to be 0.041 μM, 0.023 μM, and 0.0027 μM, respectively. The effect of some organic molecules and some metal ions on RTN detection at CMB/GNPs-CBCPE was studied with acceptable results. The sensitivity, selectivity, steadiness, repeatability, and reproducibility of the modified sensor were studied with decent results. The practicability of CMB/GNPs-CBCPE was verified by analyzing RTN in blood serum, urine, green tea, tomato, apple juice, and medicinal samples with adequate recoveries.

1. Introduction

Vitamins are the collection of important organic micronutrients that are essential for the growth and development, healthiness, and reproduction of living bodies and that are characteristically not generated by the living organism but are supplied through food resources. Vitamins are essential for the enzymatic behaviors in living bodies. Each vitamin has a distinctive role to support the body to work properly. Some vitamins are helpful to keep nerves nutritious by resisting infections in the body, though others might help to procure energy. RTN, also named rutoside or vitamin P is one of the highly effective bioflavonoids or plant pigments, this is most abundantly found in numerous plant resources, such as fruits, vegetables, and plant extracts. The RTN concentration in some real samples is found to be 0.645 mg/100 g in apple, 1.46 mg/100gm in green Tea, 0.55 mg/100 g in tomato, 0.82 mg /100 g in orange, 0.68 mg/100gm in onion, 50 to 1000 mg in medications and so on [1].

Chemically, rutin (RTN, 3′,4′,5,7-Tetrahydroxy-3-[α-L-rhamnopyranosyl-(1 → 6)-β-D-glucopyranosyloxy] flavone) is the glycoside composed by the flavonolic quercetin and disaccharide rutinose[2]. Intake of RTN rich foods during day-to-day nourishment provides promising health-related biological and pharmacological benefits, such as anti-inflammatory, antioxidant, antiviral, antibacterial, anticancer, anticarcinogenic, antidiabetic, antiprotozoal, antiallergic, antiulcer, antihypertensive, antiaging, antiadipogenic, cardioprotective, neuroprotective, vasoprotective, cytoprotective, and immunomodulator in the living bodies [3–6]. Due to these advantages, it has been applied clinically as a medicinal drug worldwide and is also used in the food, beverages, and cosmetic industries [7,8].Nonetheless, the higher quantity of RTN supplements (more than 4 g/day) conceivably causes some side effects to the living body, such as stomach upset, headache, variations in a heartbeat, high WBC counts, blurred vision, nervousness, fluid accumulation in the knees, mussel tightness, and some skin problems [9]. Hence, the analysis of RTN in food, biological

* Corresponding author.
E-mail address: manju1853@gmail.com (J.G. Manjunatha).

https://doi.org/10.1016/j.jelechem.2022.116388
Received 7 March 2022; Received in revised form 14 April 2022; Accepted 3 May 2022
Available online 06 May 2022
1572-6657/© 2022 Elsevier B.V. All rights reserved.

Colloids and Surfaces A: Physicochemical and Engineering Aspects 626 (2021) 127042

Contents lists available at ScienceDirect

Colloids and Surfaces A: Physicochemical and Engineering Aspects

journal homepage: www.elsevier.com/locate/colsurfa

A fast and selective electrochemical detection of vanillin in food samples on the surface of poly(glutamic acid) functionalized multiwalled carbon nanotubes and graphite composite paste sensor

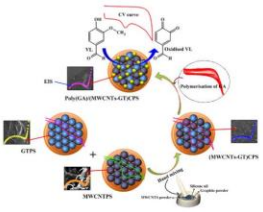
N. Hareesha [a], J.G. Manjunatha [a,*], B.M. Amrutha [a,b], N. Sreeharsha [c,d], S. M. Basheeruddin Asdaq [e], Md. Khalid Anwer [f]

[a] Department of Chemistry, FMKMC College, Constituent College of Mangalore University, Madikeri, Karnataka, India
[b] Department of Chemistry, N.M.A.M. Institute of Technol ogy, Visvesvaraya Technological University, Nitte, Udupi District, Belgavi, Karnataka 574110, India
[c] Department of Pharmaceutical Sciences, College of Clinical Pharmacy, King Faisal University, Al-Ahsa 31982, Saudi Arabia
[d] Department of Pharmaceutics, Vidya Siri College of Pharmacy, Off Sarjapura Road, Bengaluru 560 035, Karnataka, India
[e] Department of Pharmacology, College of Pharmacy, AlMaarefa University, Riyadh, Saudi Arabia
[f] Department of Pharmaceutics, College of Pharmacy, Prince Sattam Bin Abdulaziz University, Al-Alkharj 11942, Saudi Arabia

HIGHLIGHTS

- Poly(glutamic acid) functionalized multi-walled carbon nanotubes and graphite composite sensor was developed.
- Developed sensor materials were characterised using FE-SEM, EIS, and CV measurements.
- Functionalised nano-composite sensor was more sensitive and selective for vanillin detection.
- Equipped composite sensor gives a fine linear dynamic range for the oxidation of vanillin with a low limit of detection.
- The modified sensor yields adequate recoveries for vanillin in different food samples.

GRAPHICAL ABSTRACT



ARTICLE INFO

Keywords:
Electro-oxidation of vanillin
Carbon nano composite sensor
Electrochemical impedance spectroscopy
Effect of temperature
Poly(glutamic acid)
Voltammetry

ABSTRACT

The electrochemical oxidation of vanillin (VL) in 0.2 M phosphate buffer (PB) solution of pH 6.5 was determined in food samples using an electrochemically polymerized glutamic acid (GA) functionalized multiwalled carbon nanotubes (MWCNTs) and graphite (GT) composite paste sensor (CPS). The surface concert and morphology of the sensing materials were examined using field emission scanning electron microscopy (FE-SEM), electrochemical impedance spectroscopy (EIS), and cyclic voltammetry (CV) measurements. The electrochemical oxidation kinetics of VL was discussed using parameters like solution pH, potential scan rate, temperature, and accumulation time. The selective electrochemical oxidation of VL was analyzed in the presence of metal ions, organic dyes, and sugars on the surface of the functionalized composite sensor. The modified sensor provided a fine linear dynamic range (0.50–18.0 μM) for the electrochemical oxidation of VL with a low limit of detection (LOD) of 0.0199 μM. The DPV measurement was performed for the analysis of VL in food samples on the surface

* Corresponding author.
E-mail address: manju1853@gmail.com (J.G. Manjunatha).

https://doi.org/10.1016/j.colsurfa.2021.127042
Received 7 May 2021; Received in revised form 15 June 2021; Accepted 16 June 2021
Available online 23 June 2021
0927-7757/© 2021 Elsevier B.V. All rights reserved.

Journal of Science: Advanced Materials and Devices 5 (2020) 502–511

Contents lists available at ScienceDirect

Journal of Science: Advanced Materials and Devices

journal homepage: www.elsevier.com/locate/jsamd

Original Article

A simple and low-cost poly (DL-phenylalanine) modified carbon sensor for the improved electrochemical analysis of Riboflavin

N. Hareesha, J.G. Manjunatha*

Department of Chemistry, FMKMC College, Constituent College of Mangalore University, Madikeri, Karnataka, India

ARTICLE INFO

Article history:
Received 15 May 2020
Received in revised form
12 August 2020
Accepted 20 August 2020
Available online 27 August 2020

Keywords:
Riboflavin
DL-Phenylalanine
Heterogeneous rate constant
Impedance study
Voltammetry

ABSTRACT

The current study reports on the electroanalysis of Riboflavin (RF) on the surface of a poly DL-phenylalanine modified carbon paste sensor (PDLPAMCPS). The developed sensor caused a noticeable electrocatalytic action for the redox activity of RF in a phosphate buffer solution (PBS) of pH 6.5. This analysis was evaluated using differential pulse voltammetry (DPV) and cyclic voltammetry (CV) techniques. The active surface of the functioning sensor exposes well developed anodic peak with prominent electron transfer. PDLPAMCPS shows distinctive and improved DPV and CV peaks for RF with and without the presence of organic dyes and dopamine (DA). The impact of the solution pH, scan rate, accumulation potential and concentration on RF at PDLPAMCPS were studied. A vibrant linear growth was observed between the oxidation peak current and the RF concentration in the range of 6.0 μM–30.0 μM, which provides a lower limit of detection (LOD) of 92 nM with excellent sensitivity. The proposed method and sensor were applied for the assessment of RF in medicine sample as an analytical application with fine recoveries and low LOD.

© 2020 The Authors. Publishing services by Elsevier B.V. on behalf of Vietnam National University, Hanoi.
This is an open access article under the CC BY license (http://creativecommons.org/licenses/by/4.0/).

1. Introduction

RF (Vitamin B2) is an essential water-soluble organic molecule that occurs in two main co-enzymes of flavonoids found in many food resources. RF belongs to the vitamin B family, which is necessary for health, energy and tissue maintenance. According to the Oregon State University, University of Maryland Medical Center (UMM) and other Universities, the daily intake of RF for normal men and women is about 1.30 mg/day and 1.10 mg/day, respectively. Women during pregnancy should have 1.4 mg/day and during breastfeeding they need 1.6 mg/day [1]. Maintenance of this RF concentration level in the healthy living body exposes some imperative applications, such as maintenance of mucous membranes in the digestive system, maintenance of the health of external and internal organs of human (liver, eye, nerves, skin, and muscles), conversion of tryptophan (amino acid) into niacin (vitamin B3), absorption and activation of ion, folic acid and vitamins B1, B3 and B6, prevention of cataract development and conversion of carbohydrates into adenosine triphosphate (ATP) as an energy producer. RF exposes some antioxidant and anticancer activities as well [2]. However, insufficiency in the concentration of RF in the living cells, called ariboflavinosis, causes cancer-related diseases (anemia-iron deficiency in the blood), mouth ulcers, cheilosis, inflammation of the tongue, itchy eyes and some hereditary disabilities during pregnancy. In rare cases, an excess quantity of RF can damage the liver in human bodies [3,4].

According to the Linus Pauling Institute and the University of Maryland Medical Centre, the increase and decrease of DA concentration mainly depend on B vitamins such as RF (B2), B6, B12, B1, B3 and B9. Therefore, selective and sensible inspection of RF with DA is most advantageous. In the literature various analytical methods were reported for the analysis of RF: UV-spectrophotometry [5], high-performance liquid chromatography [HPLC] [6], reversed-phase-high-performance liquid chromatography [RP-HPLC] [7], capillary zone electrophoresis [8], reversed-phase liquid chromatography [9] and mass spectrometry [10]. But in certain conditions, these techniques are problematic, time-consuming and monotonous and they need costly instrumentation. They require various stages of sample preparation such as hydrolysis, washing, extraction and adaptability testing. These methods also provide higher LOD values with lower sensitivity. Therefore, these methods are less appropriate for the routine analysis of RF. Conversely, electrochemical techniques are more

* Corresponding author.
E-mail address: manju1853@gmail.com (J.G. Manjunatha).
Peer review under responsibility of Vietnam National University, Hanoi.

https://doi.org/10.1016/j.jsamd.2020.08.005
2468-2179/© 2020 The Authors. Publishing services by Elsevier B.V. on behalf of Vietnam National University, Hanoi. This is an open access article under the CC BY license (http://creativecommons.org/licenses/by/4.0/).

scientific reports

Check for updates

OPEN

Electro-oxidation of formoterol fumarate on the surface of novel poly(thiazole yellow-G) layered multi-walled carbon nanotube paste electrode

N. Hareesha & J. G. Manjunatha✉

The current study explicates the electro-oxidation behavior of formoterol fumarate (FLFT) in the presence of uric acid (UA) on the surface of poly thiazole yellow-G (TY-G) layered multi-walled carbon nanotube paste electrode (MWCNTPE). The modified (Poly(TY-G)LMWCNTPE) and unmodified (MWCNTPE) electrode materials were characterized through electrochemical impedance spectroscopy (EIS), field emission scanning electron microscopy (FE-SEM), and cyclic voltammetry (CV) approaches. The characterization data confirms the good conducting and electrocatalytic nature with more electrochemical active sites on the Poly(TY-G)LMWCNTPE than MWCNTPE towards the FLFT analysis in the presence of UA. Poly(TY-G)LMWCNTPE easily separates the two drugs (FLFT and UA) even though they both have nearer oxidation peak potential. The electro-catalytic activity of the developed electrode is fast and clear for FLFT electro-oxidation in 0.2 M phosphate buffer (PB) of pH 6.5. The Poly(TY-G)LMWCNTPE offered a well-resolved peak with the highest electro-oxidation peak current at the peak potential of 0.538 V than MWCNTPE. The potential scan rate and oxidation peak growth time studies show the electrode reaction towards FLFT electro-oxidation is continued through a diffusion-controlled step. The variation of concentration of FLFT in the range from 0.2 to 1.5 µM (absence of UA) and 3.0 to 8.0 µM (presence of UA) provides a good linear relationship with increased peak current and a lower limit of detection (LOD) values of 0.0128 µM and 0.0129 µM, respectively. The prepared electrode gives a fine recovery for the detection of FLFT in the medicinal sample with acceptable repeatability, stability, and reproducibility.

Among today's generation, a considerable number of people are suffering from lungs related health issues, such as asthma, lung cancer, chronic obstructive pulmonary disease, influenza-related infections, respiratory failure, severe acute respiratory syndrome, pneumonia, tuberculosis, and middle east respiratory syndrome[1,2].

Asthma is the most common incurable and long-lasting inflammatory infection in the routes of the lungs, which causes erratic breathing problems to humans of all ages. Asthmatic patients suffer from irritable breathing difficulties, due to puffy and inflamed airways, chest tightness, shortness of breathing, heavy coughing, and reversible airflow obstruction[3]. Over 339 million people are suffering from asthma and more than 80% of deaths are occurring due to asthma-related problems in low and lower-middle-income countries. Even though it is not curable but giving an amalgamation of inhaled corticosteroids can control asthma by preventing the loss of lung functions. The clearing and relaxing of the muscles of airways of lungs take place to improve breathing by intake of long-acting beta-adrenoceptor agonists medications specifically like salmeterol and FLFT. Also, the COVID-19 epidemic is so scary for asthmatic patients, it is essential to know that presently there is no confirmation of increased infection rates in asthma patients. Only one article reveals that asthma can upsurge the hospitalization from COVID-19 in adults (this data is based on a small number of patients)[4]. While considering the data from New York it reveals that asthma was defending the persons who died from COVID-19[5]. FLFT is also termed as (E)-but-2-enedioic acid; N-[2-hydroxy-5-[(1R)-1-hydroxy-2-[[(2R)-1-(4-methoxyphenyl) propan-2-yl] amino] ethyl] phenyl] formamide, is a salty fumarate of formoterol. FLFT is a long-acting and

Department of Chemistry, FMKMC College, Constituent College of Mangalore University, Madikeri, Karnataka, India. ✉email: manju1853@gmail.com

Journal of Electroanalytical Chemistry 878 (2020) 114533

Contents lists available at ScienceDirect

Journal of Electroanalytical Chemistry

journal homepage: www.elsevier.com/locate/jelechem

Fast and enhanced electrochemical sensing of dopamine at cost-effective poly(DL-phenylalanine) based graphite electrode

N. Hareesha, J.G. Manjunatha *

Department of Chemistry, FMKMC College, Constituent College of Mangalore University, Madikeri, Karnataka, India

ARTICLE INFO

Article history:
Received 13 May 2020
Received in revised form 13 July 2020
Accepted 27 July 2020
Available online 03 August 2020

Keywords:
Ascorbic acid
Dopamine
Heterogeneous rate constant
Organic dyes
Poly (DL-phenylalanine)
Uric acid
Voltammetry

ABSTRACT

In the present study, a sensitive and a low-priced electrochemically polymerized DL-phenylalanine graphite electrode (Poly(DLPA)-GE) wasdesigned for Dopamine (DA) sensing. The redox activity of DA was inspected at this developed electrode via cyclic voltammetry (CV) and differential pulse voltammetry (DPV) in a phosphate buffer (PB) with pH 6.5. The achieved voltammetric result presents that Poly(DLPA)-GE exposes a significant enrichment in DA redox currents with the declining of overpotential than the bare graphite electrode (BGE). In the optimal operating conditions, Poly(DLPA)-GE describes a fine linear enhancement for DA oxidation in the concentration range of 2.0 μM to 45.0 μM with an estimated lower limit of detection (LOD) of 28 nM and limit of quantification (LOQ) of 93 nM. The proposed electrode shows fine selectivity and sensitivity for DA analysis in the presence of interfering moieties such as Ascorbic acid (AA), Uric acid (UA) and organic dyes. Finally, the sensor was effectively verified for the actual DA detection in the madicinal sample.

© 2020 Elsevier B.V. All rights reserved.

1. Introduction

Neurotransmitters (NTRs) are the endogenous organic chemical messengers, which facilitate the neurotransmission between neurons and neurons to muscle tissues. NTRs play a key part in shaping our routine life and functions. Their exact statistics are indefinite, nonetheless more than 200 chemical messengers have been distinctively recognized [1,2]. DA or 3-hydroxytyramine is a vital excitatory neurotransmitter and neuromodulator in the central nervous system of mammals, which belongs to the phenethylamine and catecholamine families. DA plays an imperious role in the functioning of adrenal glands also known as suprarenal glands, that belong to the endocrine system and is accountable for the discharge of hormones that normalize the function of immune system, metabolism, balance of salt-water in the blood and cardiovascular system [3,4]. DA undergoes oxidation and autoxidation in the body, where oxidation of DA is catalyzed through an oxidoreductase enzyme by direct reaction with oxygen, generating quinones and free radicals. Due to these actions, DA shows health-related anomalies in the mammals [5]. The insufficient or excess quantity of DA develops some abnormal indications in the mammals such as muscle cramps, loss of balance, constipation, weight loss or weight gain, gastroesophageal reflux disease (GERD), disturbed sleep, low energy, inability to focus, feeling demotivated, suicidal thoughts, low or intense sexual feeling, hallucinations, aggression, lack of insight, which leads to depression, schizophrenia, Huntington's chorea, psychosis, Parkinson's disease, burning mouth syndrome, euphoria, fibromyalgia and restless legs syndrome [6,7]. Hence, the assessment of DA with AA and UA is most beneficial.

There are extensive analytical approaches for the determination of DA, such as capillary electrophoresis [8,9], electrochemiluminescence [10], high-performance liquid chromatography [11] and fluorescence [12]. In various circumstances, these methods are time-consuming, tedious and expensive, since they need several steps for sample preparation, such as washing, hydrolysis, adaptive testing and extraction. These drawbacks give a platform to build up an innovative and easy tool with better performance for DA sensing. Nevertheless, the electrochemical methods are the best adaptable and widely used methods for the testing of biological active moieties, medical diagnosis, purity of pharmaceutical samples, quality of food, soil and water, because of their high sensibility, selectivity, small expense, flexibility, excellent response and easily accessible[13–25]. Electrochemical methods are the appropriate practical methodologies with suitable working electrode materials because they are quick, specific and sensitive [26–37]. During the sensitive and selective electrochemical investigation of bioactive molecules, graphite paste sensor has been generally selected, due to their probability of modification by several chemical modifiers, fine reproducibility, implementation of stable and fine resolution voltammograms, low-cost and easy preparation method. Hence, graphite paste is

* Corresponding author.
E-mail address: manju1853@gmail.com. (J.G. Manjunatha).

http://dx.doi.org/10.1016/j.jelechem.2020.114533
1572-6657/© 2020 Elsevier B.V. All rights reserved.

Journal of ELECTRONIC MATERIALS
https://doi.org/10.1007/s11664-020-08616-7
© 2021 The Minerals, Metals & Materials Society

ORIGINAL RESEARCH ARTICLE

Electrochemical Analysis of Indigo Carmine in Food and Water Samples Using a Poly(Glutamic Acid) Layered Multi-walled Carbon Nanotube Paste Electrode

N. HAREESHA,[1] J.G. MANJUNATHA ,[1,3] B.M. AMRUTHA,[1,2] P.A. PUSHPANJALI,[1] M.M. CHARITHRA,[1] and N. PRINITH SUBBAIAH[1]

1.—Department of Chemistry, FMKMC College, Mangalore University Constituent College, Madikeri, Karnataka, India. 2.—Department of Chemistry, N.M.A.M. Institute of Technology, Visvesvaraya Technological University, Nitte, Udupi District, Belgavi, Karnataka 574110, India. 3.—e-mail: manju1853@gmail.com

Some colourants are hazardous to living organisms. Hence, a powerful and fast methodology is required for the analysis of those colourants in food and water samples. A modest electrochemically polymerised glutamic acid layered multi-walled carbon nanotube paste electrode [P(GA)LMWCNTPE] was functionalised for the sensing of indigo carmine (IC) by the differential pulse voltammetry (DPV) and cyclic voltammetry (CV) approaches. Within the optimised experimental conditions, the P(GA)LMWCNTPE holds an acceptable and high rate of electro-catalytic activity towards the redox behaviour of IC. The projected P(GA)LMWCNTPE shows a decent selectivity for IC in the presence of methyl orange. The modified sensor shows an acceptable linear growth between oxidative peak current and concentration in both CV and DPV methods with fine limit of detection values of 4.2 μM and 0.36 μM, respectively. Additionally, the developed sensor was effectively applied to detect IC in food and water samples. The morphological and surface activities of the modified and unmodified electrodes were determined through field emission scanning electron microscopy, electrochemical impedance spectroscopy, and CV techniques. The P(GA)LMWCNTPE requires a simple preparation procedure and is low-cost, with acceptable storage stability, sensitivity, and reproducibility.

(Received September 2, 2020; accepted November 6, 2020)

Published online: 04 January 2021

Monatshefte für Chemie - Chemical Monthly
https://doi.org/10.1007/s00706-021-02870-z

ORIGINAL PAPER

Electrochemical sensing of antibiotic drug amoxicillin in the presence of dopamine at simple and selective carbon paste electrode activated with cetyltrimethylammonium bromide surfactant

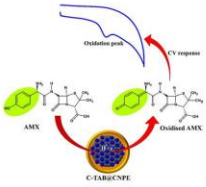
N. Hareesha[1] · J. G. Manjunatha[1] · P. A. Pushpanjali[1] · N. Prinith Subbaiah[1] · M. M. Charithra[1] · N. Sreeharsha[2,3] · S. M. Basheeruddin Asdaq[4] · Md. Khalid Anwer[5]

Received: 1 October 2021 / Accepted: 2 November 2021
© Springer-Verlag GmbH Austria, part of Springer Nature 2021

Abstract

The effective, selective, and electrochemically steady cetyltrimethylammonium bromide drop-casted carbon paste electrode was constructed for the detection of amoxicillin in presence of dopamine through cyclic voltammetry method. The modified and unmodified electrode materials were characterized by various methods like field emission scanning electron microscopy, cyclic voltammetry, and electrochemical impedance spectroscopy with acceptable results. The constructed modified sensor delivers a higher electrocatalytic nature for the oxidation of 0.1 mM amoxicillin in 0.1 M phosphate buffer saline of 6.5 pH with high peak current and lower peak potential than the bare carbon paste electrode. The analytical applicability of modified electrode for amoxicillin electro-oxidation was detected by increasing the amoxicillin concentration in the range from 10 to 150 µM with fine limit of detection and the limit of quantification of 5.90 µM and 19.67 µM, respectively. This article discloses a facile and recommended approach for the concurrent inspection of amoxicillin in the presence of dopamine. The modified sensor gives high stability, repeatability, reproducibility, and sensitivity. The premeditated method and modified sensor give a fine recovery for amoxicillin detection in medication sample.

Graphical abstract



Keywords Amoxicillin · Carbon paste electrode · Surfactant modification · Electrochemical impedance spectroscopy · Voltammetry · Electron transfer · Sensors · Dopamine

✉ J. G. Manjunatha
manju1853@gmail.com

[1] Department of Chemistry, FMKMC College, Constituent College of Mangalore University, Madikeri, Karnataka, India

[2] Department of Pharmaceutical Sciences, College of Clinical Pharmacy, King Faisal University, Al Hofuf 31982, Al-Ahsa, Saudi Arabia

[3] Department of Pharmaceutics, Vidya Siri College of Pharmacy, Off Sarjapura Road, Bengaluru, Karnataka 560 035, India

[4] Department of Pharmacy Practice, College of Pharmacy, AlMaarefa University, Riyadh, Saudi Arabia

[5] Department of Pharmaceutics, College of Pharmacy, Prince Sattam Bin Abdulaziz University, Al-Alkharj 11942, Saudi Arabia

Published online: 16 November 2021

Journal of the Iranian Chemical Society
https://doi.org/10.1007/s13738-020-01876-4

ORIGINAL PAPER

Elevated and rapid voltammetric sensing of riboflavin at poly(helianthin dye) blended carbon paste electrode with heterogeneous rate constant elucidation

N. Hareesha[1] · J. G. Manjunatha[1]

Received: 14 December 2019 / Accepted: 12 February 2020
© Iranian Chemical Society 2020

Abstract

The potent, selective, and consistent electrochemically polymerized helianthin dye modified carbon paste electrode (PHLDMCPE) was generated for the assessment of the significant antioxidant riboflavin (RL) with ascorbic acid (AA) and tyrosine (TR) using cyclic voltammetric (CV) and differential pulse voltammetric (DPV) techniques. The PHLDMCPE explicates a superior electrocatalytic resolution for the redox activity of 1×10^{-4} M RL in 0.1 M phosphate buffer solution (PBS) of pH 7.0 than the bare carbon paste electrode (BCPE). The oxidation peak current of RL and concentration of RL were attained linearly in the range of 60 μM to 150 μM with the lower limit of detection (LOD) of 4.02×10^{-8} M and the limit of quantification (LOQ) of 13.42×10^{-8} M, respectively. The heterogeneous rate constant for the equipped sensor was detected for RL at variable scan rates. This work conveys a modest and advisory methodology for the concurrent investigation of RL with AA and TR. The studied CV technique and developed sensor were adopted for the assessment of RL in pharmacological medication as a real sample.

Graphic abstract

Electrochemically polymerized HLD modified carbon paste electrode was exposed for the evaluation of antioxidant riboflavin in both real and commercial samples in optimum circumstances using CV and DPV techniques. The selective resolution and interference study of riboflavin were done with ascorbic acid and tyrosine. The surface morphology of modified and unmodified carbon sensors was studied using FE-SEM and CV methods. The modified sensor exposes refined stability, reproducibility, and repeatability with a low LOD (4.02×10^{-8} M).

✉ J. G. Manjunatha
manju1853@gmail.com

[1] Department of Chemistry, FMKMC College, Constituent College of Mangalore University, Madikeri, Karnataka, India

Published online: 20 February 2020

ChemPubSoc Europe

DOI: 10.1002/slct.201900794

Chemistry SELECT Full Papers

Analytical Chemistry

Sensitive and Selective Electrochemical Resolution of Tyrosine with Ascorbic Acid through the Development of Electropolymerized Alizarin Sodium Sulfonate Modified Carbon Nanotube Paste Electrodes

N. Hareesha, J. G. Manjunatha,* C. Raril, and Girish Tigari[a]

An approachable and a selective electrocatalytic investigation of tyrosine (TR) with ascorbic acid (AA) in phosphate buffer solution (PBS) was done using a sensitive Poly Alizarin sodium sulfonate modified Carbon nanotube paste electrode (PASSMCNTPE). The morphological and elemental studies on PASSMCNTPE and bare carbon nanotube paste electrode (BCNTPE) were resolute through field emission scanning electron microscopy (FESEM) and energy dispersive X-ray spectroscopy (EDX). The PASSMCNTPE shows excellent sensitivity, selectivity, stability, repeatability, and reproducibility for the electrochemical characterization of TR through cyclic voltammetry (CV) and differential pulse voltammetry (DPV). The prepared sensor provides an elevated current response towards TR as compared to the BCNTPE. A plot of the anodic peak current of TR and the concentration of TR was obtained linearly in the range 1.4×10^{-4} M to 2×10^{-4} M with the limit of detection (LOD) 7.8×10^{-7} M and the limit of quantification (LOQ) 26×10^{-7} M respectively. The equipped sensor was also helpful for the quantitative and qualitative analysis of TR moiety in a pharmaceutical drug as a real sample.

Introduction

TR and AA are the most imperative fundamental moieties for the living organisms. TR is one of the conditional aromatic amino acid, which is found in numerous foodstuffs; also it is a precursor for the hormones, neurotransmitters, pigments and some needful proteins.[1–3] TR reveals many applications in the human body such as improvement of mental efficiency, maintenance of positive nitrogen balance,[4] photosynthesis, normalization of high blood pressure, curing of Parkinson's disease and Alzheimer's disease.[5,6] But an abnormality of TR in the living organisms causes high blood pressure, albinism, stress, lowering of body temperature, and some thyroid problems.[7,8] AA is also named as Vitamin C, is found in many food resources and utilized for some dietary supplements. AA has numerous utilities in the living bodies such as antioxidant properties, prevention of wounds, fabrication of some neurotransmitters, and curing of bone disorder (osteogenesis).[9–11] AA exposes some effects in the body such as gastric problems, scurvy, cardiovascular disease and Alzheimer's disease.[12,13] The structure of AA is shown in Scheme 1A.

Various techniques were reported for the examination of TR such as fluorimetry,[14] gas chromatography-mass spectrometry,[15] liquid chromatography-tandem mass spectrometry,[16] chemiluminescence,[17] spectrometric analysis,[18] and capillary electrophoresis,[19] but these methods were time consuming, tedious and costly as compare to electrochemical methods.[20–23] The electrochemical methods mainly depends on modified sensors, recent works presented many modified sensors likely Europium hexacyanoferrate film,[5] Boron-doped diamond electrode,[24] Nanostructures on gold electrodes,[25] Carbon electrode modified with a Nafion/TiO2-graphene composite film,[26] Poly (thionine) glassy carbon electrode,[27] Boron-doped diamond and diamond nanowire electrode.[28] They shows comparable detection limit with lesser activity. Hence our work is mainly focused towards the development of high sensing sensor for the electrochemical analysis of TR.

Electrochemical methods have been broadly used as approachable and selective analytical techniques for the analysis of the trace quantity of biologically significant samples, pharmaceutical moieties, and food samples based on chemically modified carbon based electrochemical sensors (CMCBES). The best properties of CMCBES are catalytic activity, determination of target moieties in presence of any other active species and they are very needful in the field of medicine.[29–41]

Now a day's Carbon nanotube (CNT) paste electrodes has a wide range of applications in the electrochemical investigation of electroactive species due to its prominent mechanical strength, high electrical conductivity, larger surface area, first-class chemical stability and distinctive electronic properties,[3,42,43] hence CNT was used as a main precursor for this work.

The Alizarin sodium sulfonate (ASS) or alizarin red-S is a water soluble aromatic quinine derivative with two OH groups, which acts as a coloring agent, pH indicator, surface modifier and artificial electron donor due to these characters electro-

[a] N. Hareesha, Dr. J. G. Manjunatha, C. Raril, G. Tigari
Department of Chemistry, FMKMC College, Constituent College Mangalore University, Madikeri, Karnataka, India
Tel.: +91- 08272228334
E-mail: manju1853@gmail.com

Supporting information for this article is available on the WWW under https://doi.org/10.1002/slct.201900794

© 2019 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim

MATERIALS RESEARCH INNOVATIONS
https://doi.org/10.1080/14328917.2019.1684657

Taylor & Francis
Taylor & Francis Group

Check for updates

Surfactant and polymer layered carbon composite electrochemical sensor for the analysis of estriol with ciprofloxacin

Nagarajappa Hareesha and Jamballi G Manjunatha

Department of Chemistry, FMKMC College, Constituent College of Mangalore University, Madikeri, India

ABSTRACT

This article exposes an approachable strategy for the responsive electrochemical analysis of estriol (ER) hormone by designing a sensitive and selective sensor of sodium dodecyl sulphate and polymerised xanthacridinum modified carbon nanotube and graphite composite paste electrode (SDS-PXAMCNTGCPE) via linear sweep voltammetry (LSV), cyclic voltammetry (CV) and differential pulse voltammetry (DPV) techniques. ER exposed a fine resolved irreversibly oxidised peak in phosphate buffer solution (PBS) of pH 7.0. CV and DPV reveal a commendable linear relation between oxidative peak current of ER and concentration of ER in the range 2 µM to 200 µM and 10 µM to 70 µM and they provide a promising lowest limit of detection (LOD) values of 2.9×10^{-7} M and 1.9×10^{-7} M. CV and DPV techniques were also applied to examine the selectivity of ER with Ciprofloxacin (CF). The adapting capability of SDS-PXAMCNTGCPE was accountable for the lower level identification of ER in sewage water as a real sample. The proposed sensor needs an easy preparation method with low cost and it exhibits superior sensitivity, stability, repeatability, and reproducibility.

ARTICLE HISTORY
Received 30 August 2019
Accepted 8 October 2019

KEYWORDS
Estriol; carbon composite sensor; ciprofloxacin; voltammetry; xanthacridinum

Introduction

Biologically active molecules are most important to our metabolic activity; they show crucial applications as well as some hazardous defects to living organisms. Over a few decades, many works were reported on the investigation of bioactive moieties through numerous methods. Biologically active compounds exhibit electron transfer nature, and it can be advantageous to identify the level of activity in the living organisms, this electron transfer character is challenging to catch in the commercial or real samples by unmodified sensors. Hence, our work is mainly focused on the development of a sensitive chemically modified sensor for the detection of electroactive as well as bioactive molecules.

ER or 16α-hydroxyestradiol is a type of estrogen group belongs to the steroid family, produced by the placenta. ER is the most abundant sex hormone of female mammalian species; its production level enhances with respect to time while pregnancy, but in women who are not pregnant, and its concentration level is approximately untraceable [1–3]. ER presents very imperative applications during sexual cycle disorders, heart disorder, and hormone replacement therapy for menopause, reproductive process, birth control, cancer, osteoporosis, hyperandrogenism, and urogenital diseases in women [4,5]. However, the variation of ER concentration affects many difficulties to the living body, such as heart attack, blood clots, stroke, headache, irregular bleeding, sex ratio variation, weight loss, reproduction impairment, and breast cancer. Also, the biggest problem of ER is not degradable during sewage management, due to its massive release through urine, and it causes some health risk to living organisms [6–10]. Hence, the rescue of living bodies from these consequences is most significant by the analysis of the minute quantity of ER. The chemical structure of the ER is shown in Scheme 1(a).

ER was usually investigated by various techniques such as fluorescence [11,12], spectrophotometry [13], gas chromatography-mass spectrometry [14,15], capillary electrophoresis [16,17], chemiluminescence [18], micellar electrokinetic chromatography [19], high-performance liquid chromatography [20,21], and immunoassays [22,23]. These techniques are complicated, time-killing, tedious, and more expensive, because which need some sample preparation steps such as extraction, hydrolysis, cleaning, and compatibility checking. Hence, these methods are not appropriate for the routine assessment of ER hormone.

CF is a quinolone carboxylic acid, which acts as antibiotic, utilised for the bacterial infection-related treatments [24–26]. In this work which is used for the selectivity analysis with ER. The chemical structure of CF is shown in Scheme 1(b).

The electrochemical methods and chemically modified sensors explore excellent significances towards the evaluation of pharmaceutical samples, bioactive moieties, food analysis, and medicinal diagnosis, because of their faster rate analysis, simple working procedures, low cost, rapid response, high selectivity and sensitivity. Also, the utility of chemically modified sensors agreements a great tool for enhancing the lower level detection capability of electrodes and numerous efficient materials are used in the modification of bioactive sensors [27–58].

The monomer Xanthacridinum (XA) or Acriflavine is a colourant; it can be used as an antiseptic agent, bactericidal inhibitor, photosensitiser for anticancer agents and genetically active agents. It may be harmful to the eyes or nose [59,60]. Sodium dodecyl sulphate (SDS) is water-soluble anionic surfactant material is used to improve the surface area of the working electrodes and acts as a surface-active agent [61,62]. Hence, XA and SDS moieties were used as surface modifiers for this work primarily and secondarily.

CONTACT Jamballi G Manjunatha manju1853@gmail.com Department of Chemistry, FMKMC College, Constituent College of Mangalore University, Madikeri, Karnataka, India

This article has been republished with minor changes. These changes do not impact the academic content of the article.

© 2019 Informa UK Limited, trading as Taylor & Francis Group

Advanced Pharmaceutical Bulletin

Adv Pharm Bull, 2019, 9(1), 132-137
doi: 10.15171/apb.2019.016
https://apb.tbzmed.ac.ir

Research Article

Design of novel Surfactant Modified Carbon Nanotube Paste Electrochemical Sensor for the Sensitive Investigation of Tyrosine as a Pharmaceutical Drug

Nagarajappa Hareesha, Jamballi Gangadharappa Gowda Manjunatha*, Chenthattil Raril, Girish Tigari

Department of Chemistry, FMKMC College, Constituent College of Mangalore University, Madikeri, Karnataka, India.

Article info

Article History:
Received: 13 Dec. 2018
Revised: 1 Feb. 2019
Accepted: 2 Feb. 2019
epublished: 21 Feb. 2019

Keywords:
- Carbon nanotube
- Sodium dodecyl sulfate
- Tyrosine
- Voltammetry

Abstract

Purpose: The novel sodium dodecyl sulfate modified carbon nanotube paste electrode (SDS/CNTPE) was used as a sensitive sensor for the electrochemical investigation of L-tyrosine (TY).
Methods: The electrochemical analysis of TY was displayed through cyclic voltammetry (CV) and differential pulse voltammetry (DPV). The surface morphology of SDS/CNTPE and bare carbon nanotube past electrode (BCNTPE) was reviewed trough field emission scanning electron microscopy (FESEM).
Results: The functioning SDS/CNTPE shows a voltammetric response with superior sensitivity towards TY. This study was conducted using a phosphate buffer solution having neutral pH (pH=7.0). The correlation between the oxidation peak current of TY and concentration of TY was achieved linearly in CV method, in the range 2.0×10^{-6} to 5×10^{-5} M with the detection limit 729 nM and limit of quantification 2.43 µM. The investigated voltammetric study at SDS/CNTPE was also adopted in the examination of TY concentration in a pharmaceutical medicine as a real sample with the recovery of 97% to 98%.
Conclusion: The modified electrode demonstrates optimum sensitivity, constancy, reproducibility, and repeatability during the electrocatalytic activity of TY.

Introduction

L-tyrosine (TY) is one of the standard aromatic amino acid found in some foodstuffs and living organisms; it performs as a building block of the proteins.[1-3] TY is acting as an originator of neurotransmitters, pigments, and hormones such as dopamine, thyroid and melanin.[4-7] TY facilitates to improve mental performances and attentiveness or remembrance; also TY is use to avoid depression or attention deficit disorder, high blood pressure, Parkinson's disease, alcoholism, and cocaine addiction and too helpful for photosynthesis. The abnormality of TY could cause albinism, alkaptonuria, low blood pressure, low body temperature and an underactive thyroid.[8] Some people have the low intensity of TY in their bodies because of the hereditary condition called phenylketonuria due to this body do not develops amino acid called phenylalanine.[9,10]

In the previous works numerous methods were evidenced, such as chromatographic studies, mass spectroscopic studies,[11-14] spectrophotometric studies[15,16] and electrochemical studies for the determination of biologically active scaffolds, in these studies, electrochemical studies[17-22] such as cyclic voltammetry (CV) and differential pulse voltammetry (DPV) shows excellent sensitivity, and they are trouble-free to handle in the laboratory circumstances, these are used to study the kinetics of a reaction, electron and ion transfer reactions.[23] Also, these techniques mainly depends on chemically modified electrodes that are working electrodes. Here we use multi-walled carbon nanotube (MWCNT) for the preparation of the working electrode because it shows excellent sensitivity, steadiness, high electrical conductivity and high surface area towards biologically active moieties.[24] The modification of bare carbon nanotube past electrode (BCNTPE) was done using SDS as an anionic surfactant material; it gives more excellent sensitivity and stability during the adsorption of the analyte[25] due to the hydrophobic and hydrophilic behavior. Hence the analysis of TY was carried out at sodium dodecyl sulfate modified carbon nanotube paste electrode (SDS/CNTPE). CV and DPV were also used to investigate the reaction mechanism of TY in the pharmaceutical drug as a real sample. The structure and oxidative reaction mechanism of TY at the SDS/CNTPE is shown in Scheme 1.

Materials and Methods

Materials

Silicone oil, Sodium hydroxide and SDS were purchased from Nice Chemicals, India. Disodium hydrogen

***Corresponding Author:** Jamballi G. Manjunatha, Tel: +91- 08272228334, Email: manju1853@gmail.com

© 2019 The Author (s). This is an Open Access article distributed under the terms of the Creative Commons Attribution (CC BY), which permits unrestricted use, distribution, and reproduction in any medium, as long as the original authors and source are cited. No permission is required from the authors or the publishers.

ChemistrySelect

Research Article
doi.org/10.1002/slct.202200537

Chemistry Europe
European Chemical Societies Publishing

www.chemistryselect.org

Analytical Chemistry

Electrochemical Determination of Riboflavin using a Poly(Titan Yellow) Modified Carbon Nanotube Paste Electrode in the Presence of Dopamine

Hareesha Nagarajappa,[a] Jamballi G. Manjunatha,*[a] Abdullah A. Al-Kahtani,[b] Ammar M. Tighezza,[b] and Narges Ataollahi[c]

The bare carbon nanotube paste electrode (BCNTPE) is a helpful base material for the construction of different electrometric sensors for analytical purposes. The BCNTPE was chemically modified with a polymerization process using titan yellow (TY) dye for the selective determination of riboflavin (RF) in presence of dopamine (DA). A poly(titan yellow) modified carbon nanotubes paste electrode (PTYMCNTPE) has been constructed by a simple and eco-friendly procedure. The PTYMCNTPE material surface was examined by cyclic voltammetry (CV), Field emission-scanning electron microscopy (FE-SEM), electrochemical impedance spectroscopy (EIS), and differential pulse voltammetry (DPV) methods. The outcomes suggested that the modified electrode displays high electrocatalytic action for the redox reaction of RF. The limit of detection (LOD) and limit of quantification (LOQ) for the detection of RF were found to be 2.679×10^{-8} M and 8.932×10^{-8} M, correspondingly. The proposed sensor was effectively applied for the determination of RF in a pharmaceutical sample.

Introduction

Riboflavin (RF) is a significant water-soluble organic compound that appears in two co-enzymes flavonoids in numerous foodstuffs. RF is in the family of Vitamin-B and is essential for health, strength, maintenance of tissues, and energy.[1,2] Consumption of RF in a proper concentration in the living body divulges certain imperious functions, such as antioxidant and anticancer actions in numerous biological issues, upkeep of mucous membranes (in the digestive system), and health of internal and external organs (like liver, nerves, eye, muscles, and skin), conversion of carbohydrates into adenosine triphosphate and prevention of cataract development.[3] As per the University of Maryland Medical Center and Oregon State University, the day-to-day RF consumption for healthy men and women is around 1.30 mg/day and 1.10 mg/day, individually. Women during pregnancy and breastfeeding must have 1.4 mg/day and 1.6 mg/day, respectively.[4] Though, variation of these RF concentrations in the living body causes some health-related problems such as anemia, cheilosis, mouth ulcers, hereditary disabilities during pregnancy, inflammation of the tongue, and so on.[5–8] Also in some cases, excess RF amount can harm the liver in living bodies.[9] The Linus Pauling Institute and the University of Maryland Medical Centre conclude that the upsurge and reduction of the concentration of dopamine (DA) primarily depend on various vitamins including RF (Vitamin-B2). Thus, a selectivity study of RF was done in presence of DA in the present work. This information underlines the necessity of a simple and sensitive tool for the detection of RF in commercial and real samples.

Various methods have been established for the validation of RF, including high-performance liquid chromatography,[10] reversed-phase-high-performance liquid chromatography,[11] chemiluminescence,[12] spectroelectrochemical,[13] fluorescence,[14] reversed-phase liquid chromatography,[15] UV-spectrophotometry,[16] capillary electrophoresis,[17] mass spectrometry,[18] and so on. Nonetheless, in some circumstances, these methods are challenging, laborious, and tedious, provide higher LOD values with lower sensitivity, and need expensive equipment and expert operator. Contrariwise, electrochemical methods have been broadly used in drug examination due to their high sensitivity, fast response, low cost, simplicity in operation procedure, lower LOD, and high sensitivity.[19–23]

During the electrochemical assessment, carbon nanotubes (CNTs) have superior consideration in the development of sensors for the detection of various bioactive molecules as a result of their superb electrical conductivity, high synthetic dependability, fine catalytic action, more surface sites with

[a] H. Nagarajappa, Dr. J. G. Manjunatha
Department of Chemistry, FMKMC College,
Constituent College of Mangalore University, Madikeri,
Karnataka, India
Tel.: +91- 08272228334
E-mail: manju1853@gmail.com
[b] Dr. A. A. Al-Kahtani, Dr. A. M. Tighezza
Chemistry Department, College of Science,
King Saud University, P. O. Box 2455,
Riyadh, 11451, Saudi Arabia
[c] Dr. N. Ataollahi
Department of Civil,
Environmental and Mechanical Engineering,
University of Trento, Via Mesiano, 77,
38123, Trento, Italy

Supporting information for this article is available on the WWW under https://doi.org/10.1002/slct.202200537

© 2022 Wiley-VCH GmbH

CONFERENCES CERTIFICATES

ST ALOYSIUS COLLEGE (AUTONOMOUS)

MANGALURU, KARNATAKA- 575003

Re- accredited by NAAC with 'A' Grade with CGPA - 3.62
Ranked 94 in College Category - 2018 under NIRF, MHRD, Government of India
Recognized by UGC as "College with Potential for Excellence"
College with 'STAR STATUS' Conferred by DBT, Government of India

UNIVERSITÉ DE NAMUR

International Conference - NANOTECHNOLOGY 2019

Certificate

This is to certify that

~~Prof./Dr~~/Mr/~~Ms~~ Hareesha N of

FMKMC, Madikeri has Participated & Presented a Paper (~~oral~~/poster) entitled

Electrocatalytic Investigation of L-Tyrosine using Surfactant Modified Carbon Nanotube Paste Electrode-A Cyclic Voltammetry in the International Conference on NANOTECHNOLOGY–2019 "Opportunities and Challenges" organized by Undergraduate and Postgraduate Departments of Chemistry in association with the University of Namur, Belgium at St Aloysius College, Mangaluru on 10 & 11 January 2019.

Dr Ronald Nazareth
Convener & HOD PG Chemistry

Prof. Rajgopal Bhat
Head, Department of Chemistry

Ms Preema Pais
Organizing Secretary

Rev. Dr Praveen Martis SJ
Principal

Mangalore University

FIELD MARSHAL K.M.CARIAPPA COLLEGE

(A Constituent College of Mangalore University)

(Recognised by UGC as College with Potential for Excellence)

National Level Conference

(Under CPE Programme)

CERTIFICATE

This is to certify that Mr. N. Hareesha *of* F.M.K.M.C College, Madikeri *has participated as* ~~*Chair person*~~ */* ~~*Resource person*~~ */* ~~*Oral Presenter*~~ */ Poster Presenter /* ~~*Delegate*~~ *in the National Level Conference on "Recent Advances in Material Science" held on 5th February 2019 organised by the Department of Chemistry, Field Marshal K. M. Cariappa College, Madikeri.*

J. G. Manjunatha

Dr. Manjunatha J. G.
Convener

Dr. T. D. Thimmaiah
Principal

INDIAN ACADEMY DEGREE COLLEGE

AUTONOMOUS

NAAC Re-accredited with A Grade | ISO 9001:2008 Certified Institution | Affiliated to Bangalore North University

DEPARTMENTS OF CHEMISTRY & BIOCHEMISTRY

NATIONAL SYMPOSIUM

Recent Advances at the Interface between Chemical & Biological Sciences

Certificate

This is to certify that Mr/Ms/Dr HAREESHA . N

of PMKMC COLLEGE, MADIKERI. *presented the poster titled :*

*in the NATIONAL SYMPOSIUM on "**Recent Advances at the Interface between Chemical and Biological Sciences**" on 29th July 2019, conducted under the Star College Programme, DBT, Government of India.*

Dr. Mahuya De Ghosh / Dr. K. Prashanthi	Dr. E. Jerome Xavier	Dr. T. Somasekhar
Symposium Coordinators	Principal	Chairman

Hennur Cross, Hennur Main Road, Bangalore - 560 043, INDIA. Tel : 080-67458900 / 9880105678 E-mail: info@indianacademy.edu.in
www.indianacademy.edu.in

JSS MAHAVIDYAPEETHA

JSS SCIENCE AND TECHNOLOGY UNIVERSITY

SRI JAYACHAMARAJENDRA COLLEGE OF ENGINEERING

MYSURU

Certificate

Second National Conference on "Advanced Materials for Health, Energy and Environment" (AMHEE-2019)

NPIU

TEQIP-III INITIATIVE

Department of Chemistry

This is to certify that Mr/Ms/Mrs/Dr. Hareesha. N

F.M.K.M.C college, Madikeri has participated in Second National Conference on Advanced Materials for Health, Energy and Environment (AMHEE-2019) held on September 6th & 7th 2019 organized by **Department of Chemistry, JSS Science and Technology University, Mysuru**, Karnataka.

He/She has presented Oral/Poster presenation.

CHEM-HUB

P. Mallu
Dr. P. Mallu
CONVENOR

B. Manoj Kumar
Dr. B Manoj Kumar
Co-Ordinator
TEQIP-III

Dr. T N Nagabhushana
Principal

VIVEKANANDA COLLEGE
OF ARTS, SCIENCE & COMMERCE

NEHRU NAGAR, PUTTUR

A unit of Vivekananda Vidhyavardhaka Sangha Puttur®

[Re-accredited at "A" Grade by the NAAC with 3.30 CGPA, Recognized as the college with potential for excellence (CPE) by the UGC
Recognized as "Mentor College" by the NAAC]

Under-Graduate & Post-Graduate Departments of Chemistry

IQAC and Association of Chemistry Teachers of Mangalore University (ACT)

One Day National Seminar

on

Current Trends in Chemical Research and Development

(CTCRD-2019)

Certificate

This is to certify that Dr./Prof./Mr./Ms. HAREESHA . N from FMKMC College, Madikeri has participated/presented a paper in One Day National Seminar on **"Current Trends in Chemical Research and Development, CTCRD-2019"** held on 18th September 2019 at Vivekananda College, Puttur.

(Prof. Krishna Karanth)
Head, Department of Chemistry
Vivekananda College, Puttur
Convener, Organising Committee, CTCRD-2019

(Dr. Peter Wilson Prabhakar)
Principal,
Vivekananda College, Puttur
Chairman, Organising Committee, CTCRD-2019

DEPARTMENT OF STUDIES IN CHEMISTRY

MANGALORE UNIVERSITY

MANGALAGANGOTHRI - 574199, KARNATAKA, INDIA

ICCM 2019

International Conference on Advances in Chemical and Materials Sciences

October 17-19, 2019

Certificate

This certificate is awarded to

Prof/Dr/Mr/Mrs/Ms. **Hareesha N.**

Department of Chemistry, FMKMC College, Madikeri

for participating as **Poster Presenter** *in International Conference on*

Advances in Chemical and Materials Sciences

held in the Department of Chemistry, Mangalore University during October 17 - 19, 2019.

Prof. Boja Poojary
Organizing Secretary, ICCM - 2019

Prof. G. K. Nagaraja
Chairman, ICCM - 2019

Prof. P. S. Yadapadithaya
Vice Chancellor

Certificate *of* Participation

Indian Society of ElectroAnalytical Chemistry

(REG. NO. MAH/MUM/1173/2006GBBSD)

gladly acknowledges that

HAREESHA NAGARAJAPPA

has participated and presented a paper/~~delivered an invited talk~~ in the international event

"Conference on Electrochemistry in Industry, Health and Environment"
(EIHE 2020),
held at
DAE CONVENTION CENTRE, ANUSHAKTINAGAR, BHABHA ATOMIC RESEARCH CENTRE, MUMBAI, INDIA
during
JANUARY 21 - 25, 2020.

INDIAN SOCIETY FOR ELECTROANALYTICAL CHEMISTRY • MUMBAI • ISEAC

Dr. H. Pal
Chairman, EIHE 2020

Dr. A. K. Satpati
Convener, EIHE 2020

Mangalore University

FIELD MARSHAL K.M.CARIAPPA COLLEGE

(A Constituent College of Mangalore University)

(Recognised by UGC as College with Potential for Excellence)

National Conference

CERTIFICATE

This is to certify that Hareesha N. *of* F.M.K.M.C. College, Madikeri *has participated as ~~Chair person~~ / ~~Resource person~~ / ~~Oral Presenter~~ / Poster Presenter / ~~Delegate~~ in the National Level Conference on "Recent Novel Approaches in Chemical Sciences" held on 12th February 2020 organised by the Department of Chemistry, Field Marshal K.M. Cariappa College, Madikeri.*

J. G.

Dr. Manjunatha J. G.
Convener

Dr. C Jagath Thimmaiah
Principal